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Investigation of Chemically Bonded Phosphate Ceramics/Cements and Applicability of Magnesium Potassium Phosphate Cements as Wellbore Sealants in the Oil & Gas Industry

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Investigation of Chemically Bonded Phosphate Ceramics/Cements and Applicability of Magnesium Potassium Phosphate Cements as Wellbore Sealants in the Oil & Gas Industry

by

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Dedication

To my beloved parents and brother for their unconditional love and support

To my friends who make my life meaningful and enjoyable

To everyone else who helped along the way

You are a great part of this work.

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Abstract

Investigation of Chemically Bonded Phosphate Ceramics/Cements and Applicability of Magnesium Potassium Phosphate Cements as Wellbore Sealants in the Oil & Gas Industry

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Cementing jobs especially in arctic regions and/or geothermal fields in the oil and gas industry pose significant challenges and demand critical mechanical properties on cements. Researchers propose that chemically bonded phosphate ceramics/cements (CBPC) can successfully be used as wellbore sealants where conventional Portland cement systems fail to meet desired properties. Chemically bonded phosphate cements can be described as rapid setting cements, which achieve the hardness and the durability of conventional cements and ceramics.

Magnesium potassium phosphate cements (MKPC) are the most developed materials in the family of chemically bonded phosphate cements. They are formed at ambient temperatures by chemical reactions between dead burned magnesium oxide (MgO) and potassium dihydrogen phosphate (KH_2PO_4). In general, they exhibit superior mechanical properties than Portland cement systems, and they have successfully found

applications in various fields where the benefits outweigh the costs such as radioactive/hazardous waste encapsulation, biomedical/clinical treatments, and civil engineering structural materials.

In the literature, only a few MKPC formulations have been proposed as wellbore sealants for permafrost wells by simulating the arctic conditions. In this thesis, an investigation of the applicability of chemically bonded phosphate ceramics/cements in the oil and gas industry has been conducted with a primary focus on magnesium potassium phosphate cements (MKPC). Furthermore, new MKPC formulations in compliance with American Petroleum Institute (API) standards with sufficiently long thickening time (pumping time) and enough compressive strengths have been achieved at 72 ºF temperature and at atmospheric pressure conditions by this study.

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Chapter 1: Introduction

This chapter briefly describes the aim of this thesis with the problem description and research objectives. An overview of the chapters is also provided.

PROBLEM DESCRIPTION

Today, cementing operations in the oil and gas industry demand very critical requirements on cement properties, especially the subzero temperatures encountered in wells at permafrost regions and/or super high temperatures in geothermal wells make the cementing operations even more challenging. For arctic/permafrost wells, water in the cement slurry should not freeze until the cement sets (Cameron, et al., 1971). Moreover, cement should not disturb the ice network around the wellbore in order to prevent thawing of near wellbore region and to avoid well integrity problems in the future. The freeze temperature depressants such as salts, alcohol, and polymers are commonly used to lower the freezing point of water so that cement can set even at subzero temperatures. However, they should be carefully used because excess amounts can lower the ultimate compressive strength and cause well integrity problems (Limaye, et al., 2011).

It has been proposed that magnesium potassium phosphate cements (MKPC) can be used successfully as wellbore sealants in the oil and gas industry where conventional cement systems fail to meet the critical requirements at challenging regions. They exhibit low thermal conductivities, high early strengths and good bonding characteristics to earth materials. In addition, they are formed at ambient temperatures, set in rapidly (typically in less than 1 hour), and a significant amount of heat is generated during the formation. Due to short setting time and heat of hydration encountered during formation of these cements, majority of applications are concentrated in small-scale applications (Wagh,

2016). On the other hand, thickening time (pumping time) is very important in the oil and gas industry because well cementing practices require large volumes of cement slurry to be prepared and placed in the annulus requiring a few hours - typically 2 hours to 5 hours from a practical standpoint. Up to now, a few MKPC formulations have been proposed for permafrost to shallow wells by simulating the arctic conditions in the literature. However, they have not been employed in the oil and gas industry yet. For these reasons, further research is required to better understand and characterize these cements. Then, they may have a market value as wellbore sealants in the oil and gas industry.

RESEARCH OBJECTIVES

Temperature plays a critical role in formulation of MKPC acrylic cements, and optimum amounts of additives should be present in the composition. For the oil and gas industry, it is necessary to achieve new MKPC formulations with sufficiently long thickening times, high thaw resistance, effective sealing and insulating properties with low thermal conductivity. In addition to these, cement paste should also achieve a minimum of 500 psi compressive strength at 24 hours according to API standards. After all, MKPC can be utilized successfully and safely as wellbore sealants at permafrost wells to prevent thawing of the permafrost, at wells with steam injection/production activities and at geothermal wells to prevent heat losses to surroundings due to lower thermal conductivity and superior insulating properties.

In this study, research was conducted on magnesium potassium phosphate cements. It is aimed to achieve new formulations with sufficiently long thickening times and enough compressive strengths, and applicability/feasibility of these cements as wellbore sealants in the oil and gas industry has been investigated by laboratory experiments. Myriad experiments have been conducted by mixing various proportions of

magnesium oxide (MgO), potassium dihydrogen phosphate (KH_2PO_4) and fly ash powders at 72 ºF and atmospheric pressure conditions.

REVIEW OF CHAPTERS

This thesis provides a detailed research on chemically bonded phosphate cements with a primary focus on magnesium potassium phosphate cements. It presents applications of these acrylic cements in various fields including MKPC formulations proposed for the oil and gas industry. New MKPC formulations have been developed at laboratory conditions and the applicability of them in the oil and gas industry for well cementing jobs have been investigated.

Chapter 2 introduces the main differences between ceramics and cements. It presents a general overview of chemically bonded phosphate ceramics/cements. Then, it introduces the magnesium potassium phosphate cements. Solution chemistry and resulting microstructure have been provided with factors affecting the chemical reaction kinetics.

Chapter 3 summarizes the experimental results and discussions through critical experimental findings readily available in the literature. Characteristic properties of MKPC formulations are demonstrated, and previously proposed formulations for the oil and gas industry are provided in this section.

Chapter 4 briefly describes the experimental analysis conducted by this study. Raw materials utilized in the experiments are introduced. Preparation of cement slurry and test methods is also explained in this section.

Chapter 5 is dedicated to experimental results and discussions. It discusses critical findings from experiments such as temperature evolution, cement set behavior, effects of salt on mechanical properties, and overall results for thickening time and compressive

strength. A cost analysis is also conducted in this section to investigate economic viability of these cements as wellbore sealants.

Chapter 6 presents a summary of the thesis, key results, and recommendations for future studies.

Chapter 2: Literature Review

This chapter introduces ceramics and cements. It presents a general overview of chemically bonded phosphate ceramics/cements. Then, it introduces the magnesium potassium phosphate cements. Solution chemistry and resulting microstructure have been provided with factors affecting the chemical reaction kinetics.

CERAMICS AND CEMENTS

Ceramic materials have been used in various applications. They are hard and dense materials, which are formed by sintering and fusion of powders at elevated temperatures ranging from 2,000ºC to 3,000ºC. As a result, they have a highly crystalline structure. In general, they are prepared in small quantities, and they exhibit higher strengths than cements because of the ionic and covalent bonds in their crystalline structure (Wagh, 2016).

On the other hand, Portland cement and its modifications are prepared by mixing different aggregates and fly ash powders with water at ambient temperatures. Thus, they are called hydraulic cements. When raw materials are mixed with water, the slurry sets in after some time and hardens in a solid mass. Because they are readily available and easily formed, they are usually prepared in large amounts. They have modest strengths and stiffness in compression, but they are weak in tension and lack toughness (Roy, 1987). They form chemical bonds of van der Waals among the powders, and their resulting structure is non-crystalline (Wagh, 2016).

The main difference between cements and ceramics is the way they form. While ceramics are formed by high temperature sintering (fusion and consolidation of powders at elevated temperatures), cements are formed at room temperatures by mixing the dry powders with water. Considering the cost of raw materials and cost of high-temperature

processes, ceramics are more expensive than cements, and they are mostly used in small volume applications where the benefits outweigh the costs. In addition, ceramics are more resistant to higher temperatures while cements are more susceptible to high temperatures and acidic environments. Moreover, ceramics exhibit typically less than 1% porosity, but most Portland cements show typically a porosity of 15-20% (Wagh, 2016).

CHEMICALLY BONDED CERAMICS/CEMENTS

Modifying cement compositions and manipulating the microstructures resulted in development of very strong cements, chemically bonded ceramics. The definition of chemically bonded ceramics refers to formation of ceramic like materials, which include consolidation of inorganic materials into a hardened mass by chemical reactions at ambient temperatures. In other words, their properties are like ceramics, but they are formed like cements (Wagh, 2016). Some researchers simply identify these ceramic-like materials as the products that formed a crystalline microstructure at low temperatures. Thus, some authors call them as ceramics to emphasize the highly crystalline microstructure and cements to highlight the large volume applications requiring hours for preparation, mixing, pumping and/or placing the cement slurry (Wagh, 2013). They exhibit superior properties such as fast setting, high early strength and high adhesive properties. In fact, their strengths can approach the strengths of many traditional high temperature ceramics (Roy, 1987). The excellent mechanical properties of these ceramic-cement materials; rapid setting, formation at room temperature and low cost make them viable alternatives to Portland cement in myriad applications (Wagh, 2016).

Evolution of Chemically Bonded Phosphate Ceramics

Since the invention of Portland cement by Aspdin in 1824, Portland cement and its modifications are readily accepted over high temperature sintering of ceramics, and significant research has been conducted for understanding the chemical reactions among the particles of raw materials (Wagh, 2013). In fact, it was key to produce first commercially available chemically bonded ceramic products (Sorel, 1867; Wilson, 1978). In the 19th century, chemically bonded ceramics were developed with a primary focus on dental cements due to clinical demands with high compressive strengths greater than 50MPa and setting times less than 10 minutes (Rollins, 1979; Gaylord, 1989; Driessens, et al., 2005; Wagh, 2016). Afterwards, it was understood that they can also have applications in nuclear sciences (Roy, 1987; Wagh, et al., 1999), in civil engineering structural materials (Popovics, et al., 1987; Yang, et al., 2000), in corrosion and fire protection coatings (Wagh, 2013). For this reason, several chemically bonded ceramics including phosphate ceramics, silico-phosphate ceramics, and aluminum phosphate ceramics have been investigated, and chemically bonded phosphate ceramics (CBPC) have become most common cements among these ceramics. Since then, these ceramics have attracted many researchers for their superior properties compared to Portland cement, and they have found applications in different fields (Wagh, 2016).

Many researchers have contributed to the development of CBPC while studying and explaining the chemical reactions between acid phosphates and various metal oxides that produce CBPC. In the 1990s, Argonne National Laboratory developed a magnesium phosphate ceramic formulation for radioactive and hazardous waste management purposes. Wilson and Nicholson suggested that the aluminosilicate glass could react with phosphoric acid to form a strong phosphate bonded cement (Wilson & Nicholson, 1993). Further research revealed their excellent properties such as low porosity, low

permeability (Wagh, 2013), good durability, high corrosion resistance (Wagh, 2016) and ability to set within minutes (Sarkar, 1990; Seehra, et al., 1993; Hou, et al., 2016) at temperatures as low as -20 ºC (Li & Chen, 2013), good volume stability, low drying shrinkage, excellent frost resistance and good bonding properties to steel, concrete (Qiao, et al., 2010), and to other earth materials such as limestone and sandstone. Thanks to all research activities, there are few products marketed in nuclear and civil engineering applications (Wagh, 2016).

Application of Chemically Bonded Phosphate Ceramics

It is necessary to state that although the chemically bonded phosphate ceramics exhibit excellent properties, applications of them are still limited due to the heat of hydration (formation) and short setting times during their formation (Shijian & Bing, 2014). The formation of CBPC generates heat, and the cement sets within minutes even with addition of retarders such as boric acid, borax and other boron components (Wagh, 2013). The literature review suggests that the setting time is less than 45 minutes for many formulations, which indicates very little working time to mix the ingredients, to prepare and to place the cement slurry. Nonetheless, the applications of them can be seen in the following major fields (Wagh, 2016):

- Immobilization of radioactive waste and mixed waste streams
- Nuclear shielding materials
- Corrosion and fire protection industrial coatings
- Structural products
- Dental and prosthetic cements
- Oil Field cements

These ceramic-like cements have attracted attention in radioactive waste encapsulation because of their advantage of room temperature processing (Roy, 1987). Chemical immobilization of the radioactive and hazardous contaminants, or converting them into insoluble compounds (Conner, 1990) is extensively used in CBPC technology where contaminants result in insoluble, impermeable boron-rich phosphate salts (Wagh, 2013). CBPC have been evaluated for their lighter weight and ability of boron tolerance because boron-containing CBPC can be used for safe storage and transportation of some nuclear materials. Since high amounts of boron can be added to the matrix, Eagle Picher Industries produced a composition, Borobond (a trademark of Ceradyne Corporation). They developed rack-able can storage boxes with Oak Ridge National Laboratory for safe storage of highly enriched uranium (HEU) (Ehst, 2010).

CBPC technology is applicable to most acute high activity waste and the most feasible candidate for further study and applications in this field (Wagh, 2013). Several other researchers have conducted research for immobilization of waste streams using CBPC (Cantrell & Westsik, 2011; Mattigod, et al., 2011). It has been reported that majority of large-scale applications are only seen in stabilization of toxic materials, nuclear wastes and shielding applications (Buj, et al., 2009; Covill, et al., 2011).

In addition to radioactive waste and nuclear materials encapsulation, the use of CBPC is feasible with a continuous process design for large volume applications in corrosion and fire protection coatings, insulating grouts (Wagh, 2013). More applications can also be found in natural fiber composite products (Donahue & Aro, 2010). Another example use of CBPC is roof tiles in India to reduce the temperature in houses by 8-10ºC in summer and to provide thermal insulation. Additionally, Eon Coat Inc serves as corrosion and fire resistant, environmentally friendly coatings with the technology of CBPC. Potential applications of CBPC are shown in Figure 2.1 (Wagh, 2016).

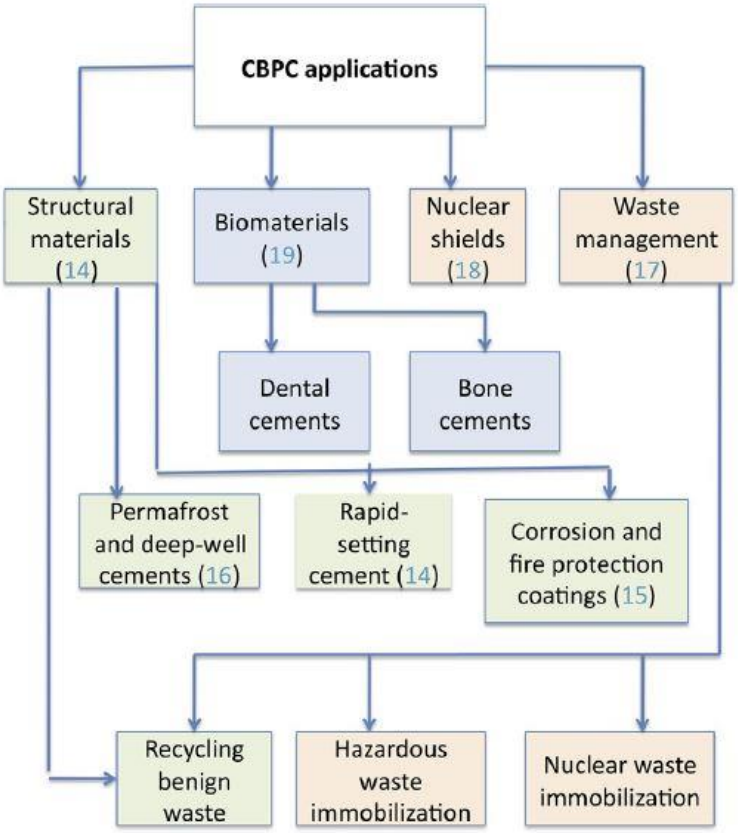

Figure 2.1: Potential applications of CBPC (Wagh, 2016).

CBPC have found applications in civil engineering as rapid repair materials such as road repair, pavement repair, building runaways etc. (Park, et al., 2016). There are commercially available products in the market. Some examples include products of companies (Péra & Ambroise, 1998; Qiao, et al., 2010) such as Bindan Corp., which manufactures commercial cement products under the Mono-Patch brand name (Mono-Patch, 2018); Grancrete Inc., which is a spray-on fire resistant cement, resistant to low to high temperatures (Grancrete, 2018); Premier Magnesia LLC (Shand, 2018). These companies serve road repair materials, concrete repair products, and floor surfacing products that are made of CBPC.

CBPC are also widely used in dental, prosthetic cements with antibacterial properties (Mestres & Ginebra, 2011) because they are phosphate-based ceramics, which match with the composition of a bone and/or teeth (Kouassi, et al., 2003). As an example, Dentsply Company utilized the research and owned root canal materials. Consequently, new companies are investing and helping the development of CBPC technology with a wide range of products in different application fields (Wagh, 2013).

Environmental Considerations of Chemically Bonded Phosphate Ceramics

According to literature, chemically bonded phosphate ceramics are reported as environmentally friendly and non-toxic cements for many applications. In this manner, the only environmental impact reported is greenhouse gas emissions to the atmosphere during extraction of the raw materials from mines and process emissions during the extraction of minerals, production operations, packaging, and transportation. It has been suggested that chemically bonded phosphate ceramics have 40% less direct emissions compared to Portland cement manufacturing process (Wagh, 2013).

MAGNESIUM POTASSIUM PHOSPHATE CERAMICS/CEMENTS

Magnesium phosphate ceramics were discovered by Prosen as materials for casting in 1939-1940s. These materials are room temperature setting ceramics with highly crystalline structure. The chemical reaction between calcined magnesium oxide (MgO) (Odler, 2000)) and an acidic water-soluble phosphate (a solution of a phosphoric acid or an acid phosphate) results in a quick setting ceramic like cement. Magnesium phosphate ceramics can be divided into groups according to the phosphate salt used. Various magnesium phosphate cements have been developed by using different phosphate salts such as ammonium phosphate, potassium phosphate, sodium phosphate

etc (El-Jazairi, 1982; Qiao, et al., 2010). Since ammonium phosphate cement has the disadvantage of producing ammonia, it has limited applications in outdoors only (Lahalle, et al., 2016). The most common phosphate studied and applied in the literature is the potassium dihydrogen phosphate (KH_2PO_4) (Park, et al., 2016; Yu, et al., 2017).

Magnesium Potassium Phosphate Ceramics/Cements (MKPC) have been developed for stabilization and encapsulation of radioactive and hazardous wastes at Argonne National Laboratory in U.S. (Wagh, et al., 2015) Since this material can set at room temperature like a concrete, it was named as Ceramicrete. It is formed by the reaction of magnesium oxide and potassium dihydrogen phosphate to develop a stronger and denser material to encapsulate/stabilize radioactive and hazardous waste streams (Torras, et al., 2011) including wastes with high potential of leaching (Wagh & Jeong, 2003; Borzunov, et al., 2004). Setting time of Ceramicrete has been reported as approximately one hour, and it can be extended by addition of boric acid and other extenders such as fly ash and/or wollastonite. Compressive strengths of Ceramicrete have been found in the range from 55MPa to 83MPa (Wagh, 2016). Furthermore, it shows high bond strengths and low drying shrinkage (Qiao, et al., 2010). According to Wagh, dead burnt magnesium oxide and potassium phosphate are the most common metal oxide and acid phosphate to produce practical CBPC. According to him, Ceramicrete with potassium dihydrogen phosphate has been the most successful commercial product because of the range of applications (Wagh, 2013) and the commercial products in American and European markets (Wagh, 2016).

Solution Chemistry and Crystal Structure

In general, the formation of CBPC requires an aqueous solution of acid phosphate and an alkaline component of sparsely (slightly) soluble oxide mineral. The acid

phosphate anions lower the pH of the solution by dissolution, and this increases the solubility of oxide cations. The reaction between anions and cations results in the formation of neutral phosphate. The formation of CBPC is an acid-base reaction. The rate of dissolution of the metal oxides is very critical to form coherent structures because high reactivity of metal oxide increases the rate of reaction, generates precipitates, but may not form coherent structures. Therefore, not all cationic metal oxides are suitable for the formation of such ceramic-cement like materials (Wagh & Jeong, 2003). The dissolution reactions for magnesium oxide and potassium dihydrogen phosphate can be written as follows (Wagh, 2013):

$$MgO \rightarrow Mg^{2+} + O^{2-}$$

$$KH_2PO_4 \rightarrow 2\ H^{+} + KPO_4^{2-}$$

$$Mg^{2+} + KPO_4^{2-} \rightarrow MgKPO4$$

$$2\ H^{+} + O^{2-} \rightarrow H_2O$$

Water is produced by the chemical reaction and some water from the solution also takes place in the final crystal structure as bound water. Importantly, some of the water evaporates during the reaction because of the heat generated during the exothermal reaction. The general reaction for the magnesium potassium phosphate cement (MKPC) can be written as follows (Gardner, et al., 2015; Wagh, 2016):

$$MgO + KH_2PO_4 + 5\ H_2O \rightarrow MgKPO_4 * 6\ H_2O$$

Magnesium oxide cations react with phosphate anions to form a crystalline structure (Wagh, 2016). The dissolution of MgO and KH_2PO_4 results in the formation of final hydration product $MgKPO_4 * 6\ H_2O$ (K-struvite), which is the main precipitated hydrate playing an essential role in the performance of MKPC (Odler, 2000). It is isostructural to struvite ($NH_4MgPO_4 * 6\ H_2O$) (Mathew & Schroeder, 1979), naturally cementitious (Gardner, et al., 2015) and highly crystalline (Wagh, 2013). It was first

discovered in Switzerland and Austria, which was classified as a distinct mineral species by the Commission of New Mineral and Mineral Names, International Mineral Association (CNMMN-IMA) (Gardner, et al., 2015). It is known as K-struvite in the mineralogical literature (Graeser, et al., 2008). Many researchers studied the K-struvite in detail because it affects the durability and performance of the cement (Hou, et al., 2016). The cementing action has been attributed to the formation of K-struvite (Ding, et al., 2012). Some researchers investigated the reaction kinetics and setting characteristics of K-Struvite, and they found some portion of unreacted magnesium oxide in most samples (Ding, et al., 2012) beside K-struvite crystal structure with bound water (Wagh, 2013). Unreacted magnesium oxide has been reported to be good for strength, integrity, fracture toughness, and crack resistant cement (Wagh, 2016). In fact, unreacted magnesium oxide grains and hydration products form a network of ionic bonds among the particles and structure becomes as dense as ceramic (Andrade & Schuiling, 2001). Moreover, it has been reported that control of particle size (with an optimum particle size) and removal of entrapped air by applying modest pressures (up to 5MPa) can generate strength and defect-free cements (Roy, 1987). Additionally, the reaction rate accelerates as magnesium oxide grains become smaller (Wagh, 2013).

To produce CBPC, the solubility of the oxide is critical because when the solubility of the oxide is too high reaction takes place in a very short time, and this allows formation of only small amounts of cement. For example, calcium oxide (CaO) solubility is too high, and the chemical reaction is very exothermic, so it only allows a little working time and results in a small amount of calcium-based ceramic formation (Wagh, 2013). In addition to oxide solubility, the phosphate solubility plays an important role during chemical reactions. Unlike other phosphates, for instance, potassium phosphate

has a lower solubility, which results in a slower reaction rate and less heat generation during the exothermic reaction (Wagh, 2016).

Magnesium Potassium Phosphate Cements (MKPC) are also frequently mixed with other binder and filler materials. They can be blended with up to 50wt.% fly ash to reduce the cost, water demand, and heat of formation. Blending with binder and fillers also helps to achieve a crack-free hardened paste (Gardner, et al., 2015). For these reasons, several researchers have studied the effects of inclusion of fly ash and other binder and filler materials on the mechanical properties of MKPC (Xing, et al., 2011).

Effect of Calcination on Solubility of Magnesium Oxide

Since the reaction takes place very fiercely in a short time, research has focused on increasing the setting time. One method to reduce the dissolution rate of magnesium oxide is calcination of MgO at high temperatures (Eubank, 1951). Eubank showed that calcination of magnesite at 1300ºC reduces the porosity of MgO particles and increases the particle size while forming periclase, which is a highly crystallized mineral at very high temperatures (Ding, et al., 2012). Wagh explained that the calcination causes a crystallization of amorphous coatings on individual grains and leads to a reduction of particle surface area; thus, the solubility and reaction rate of calcined magnesium oxide is slowed down enabling control on reactivity and setting time (Wagh, 2016).

Effect of Boron Particles on Solubility of Magnesium Oxide

Another method to slow down the reaction rate in the literature has been reported as addition of retarders to obtain a reasonable setting time. If large volumes of ceramics are aimed to produce, then some chemicals should be added to retard the chemical reactions, to control the heat of formation, and to obtain a controlled chemical reaction.

These retarders refer to boron particles, boric acid and borax minerals (Ding, et al., 2012). According to Wagh, an addition of only 1% of boric acid to a powder mixture of MgO and KH_2PO_4 can retard the setting time of the slurry from 1.4 hours to 4.5 hours (Wagh, 2016). However, some researchers have shown that high amounts of borax can result in loss of strength. Thus, optimum amounts of the borax should be added into the slurry while controlling the thickening time and mechanical properties (Yang & Qian, 2010).

Assumptions postulated regarding the mechanism of delay of chemical reactions include (i) the gradual precipitation of a coating layer of lünebergite at the surface of magnesium oxide grains, (ii) adsorption of $B(OH_3)$ at the magnesium oxide grains, and (iii) magnesium borate complex formation in the solution (Hall, et al., 2001). Lahalle et al. investigated the retardation effect of boric acid and suggested that boron remains in the solution, and boric acid does not slow down the initial dissolution of the reactants, but it retards the precipitation of the crystalline products. Moreover, his study also suggested that boric acid changes the composition of hydrated cement and tends to form $Mg_3(PO_4)_2*22H_2O$ minerals against the K-struvite formation (Lahalle, et al., 2016). On the other hand, Wagh proposed that when a small amount of boric acid is added to the system, the magnesium oxide particles are coated and prevented from dissolving in acid solution. As the pH of the solution rises, coatings are dissolved, and MgO grains start to dissolve in acid solution. Since the dissolution is delayed for some time, the reaction rate is reduced while extending the setting time (Wagh, 2016).

To increase the setting time of the ceramic, Wagh demonstrated the use of aggregates such as sand, pea gravel, and stones which absorb some of the heat generated and lower the temperature rise and slow down the reaction rate. Moreover, addition of fly ash into the slurry as a filler resulted in higher compressive strengths and that was

attributed to additional chemical reactions between acidic phosphates and amorphous silica from ash. Similarly, addition of wollastonite ($CaSiO_3$) or chopped glass fibers resulted in enhanced flexural strength (Wagh, 2013).

Effect of Excess Magnesium Oxides

The setting time of the CBPC is very sensitive to magnesium oxide content. During the Ceramicrete testing, Wagh reported that the increasing magnesium oxide content refers to an additional surface area and additional nucleation sites which enhances magnesium oxide dissolution and a faster reaction with phosphate anions. Thus, setting time is significantly reduced as the chemical reaction gets faster. Figure 2.2 shows the sensitivity of the magnesium oxide content for setting time of Ceramicrete (Wagh, 2016).

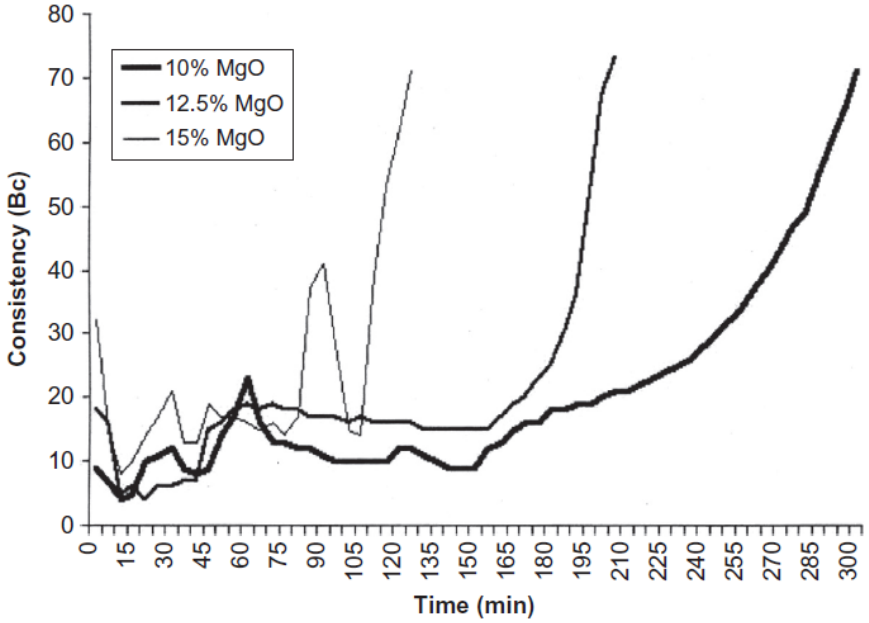

Figure 2.2: Magnesium oxide content and rate of setting reaction (Wagh, 2016).

Chapter 3: Experimental Work in The Literature

Several researchers have conducted a wide range of experiments to better understand and characterize magnesium potassium phosphate cements. This chapter summarizes the experimental results and discussions through critical experimental findings readily available in the literature. Characteristic properties of MKPC formulations and available formulations for the oil and gas industry are also provided in this section.

COMPRESSIVE STRENGTH

Magnesium potassium phosphate cements (MKPC) typically show rapid hardening and high early strengths (Limaye, et al., 2011). Compressive strength highly depends on the composition of the cement. Depending on the type of additives and their amounts in the slurry, a wide range of compressive strength can be obtained for MKPC. For example, Park investigated different magnesium to potassium (M/P) ratios and effects of borax addition. The composition of his samples is provided in Table 3.1, and compressive strength development for a variety of M/P ratios is illustrated in Figure 3.1. The control in Figure 3.1 refers to ordinary Portland cement sample. His results indicated that compressive strength changes with varying M/P ratio and highest compressive strengths were achieved with a M/P ratio of 4. Also, the samples showed higher tensile and flexural bond strengths compared to the ordinary Portland cement. It was also reported that addition of borax lowers the compressive strength (Park, et al., 2016).

Binder	Activator	Type	W/M	M/P ratio	B/M ratio	S/(M+P)
MgO	KH_2PO_4	Paste	0.2	1	Without borax	-
				4	0.02	
				8	0.04	
				12	0.08	
					0.10	
MgO	KH_2PO_4	Mortar	0.2	1	Without borax	1.5
				4	0.02	
				8	0.04	
				12	0.08	
					0.10	

Table 3.1: Mix proportion of MPC paste/mortar (Park, et al., 2016).

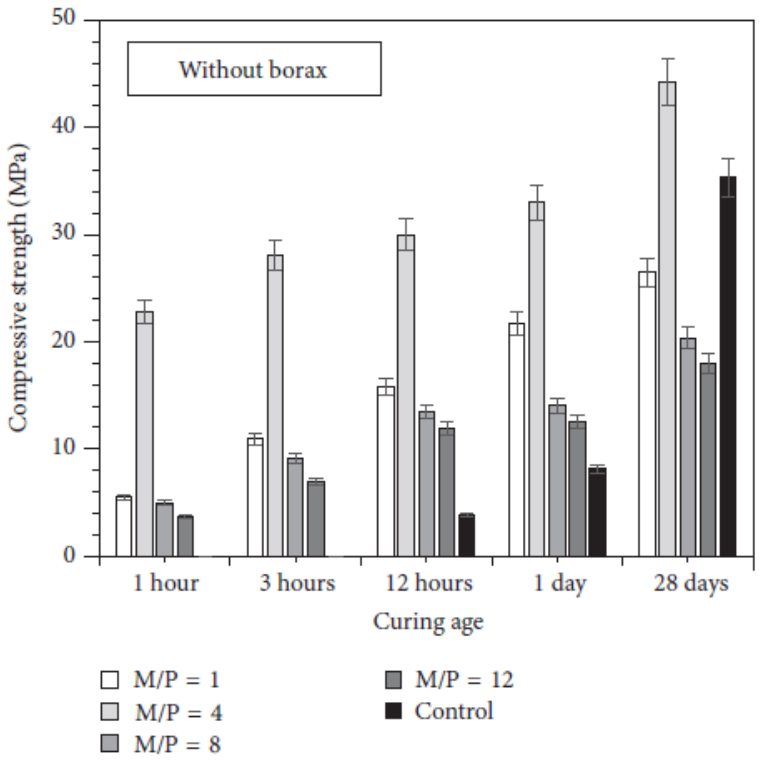

Figure 3.1: Development of compressive strength vs. various M/P ratios without borax (Park, et al., 2016).

It was also supported by Hou et al. that MKPC mechanical properties are gradually weakened with increasing M/P ratio. For further information, the composition of the mixture is provided in Table 3.2 and compressive strength results are demonstrated in Figure 3.2 for varying M/P ratios. According to Figure 3.2, compressive strength decreases as the M/P ratio increases. It was suggested that a lower M/P ratio contributes to better K-struvite crystallization by microstructure analysis. Moreover, it has been shown that as water content increases, the ultimate strength of the cement decreases (Hou, et al., 2016).

M/P ratio	MgO (g)	KDP (g)	Borax (g)	Sand (g)	Water (g)	Water/Powder ratio
18	1147.5	202.5	67.5	1350	283	0.2
12.7	1000	250	62.5	1250	262.5	0.2
9.5	937.5	312.5	62.5	1250	262.5	0.2
7.4	875	375	62.5	1250	262.5	0.2
5.9	812.5	437.5	62.5	1250	262.5	0.2
4.8	750	500	62.5	1250	262.5	0.2

Table 3.2: Mixture portion for the MPC mortars (Hou, et al., 2016).

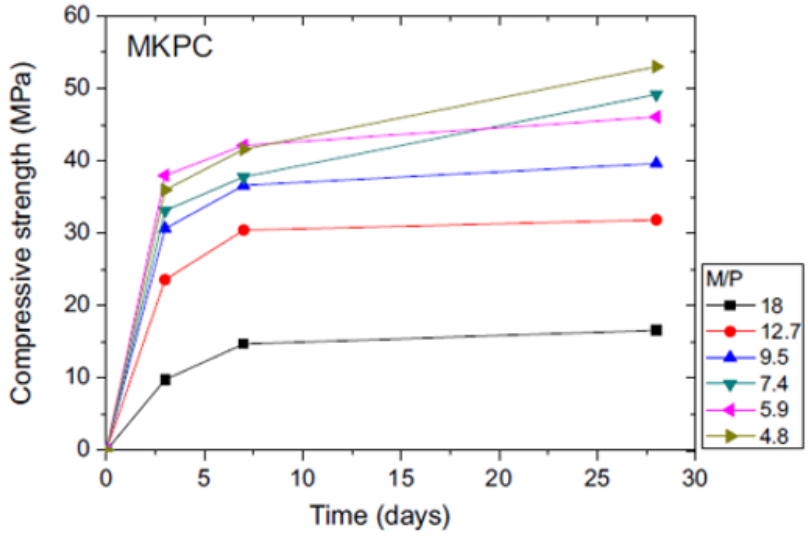

Figure 3.2: Compressive strength development at 3, 7, and 28 days for various M/P ratios (Hou, et al., 2016).

Some researchers have also studied the effect of fly ash addition. Ding and Li reported that MKPC samples with up to 40% fly ash developed nearly 36MPa compressive strength while samples without fly ash developed only 24MPa compressive strength (Ding & Li, 2005). Gardner et al. also investigated the properties of MKPCs with additives of fly ash (FA/MPKC) and granulated blast furnace slag (GBFS) to provide a detailed characterization of such binder and filler systems. Table 3.3 shows the formulations of MKPC with water to solids ratio of 0.24 studied by Gardner et al. The compressive strength results are shown in Figure 3.3. It can be seen in Figure 3.3 that FA/MKPC systems show a slightly enhanced of compressive strengths for any curing day. Moreover, it was proposed that fly ash binder and filler systems can be used to reduce heat evolution, water demand, and cost (Gardner, et al., 2015). In fact, fly ash in a MKPC system acts as an inert filler and binder. It was observed comparable compressive strength results with fly ash MKPC with available data in the literature (Covill, et al., 2011).

Blend	MgO (g)	KH_2PO_4 (g)	H_2O (g)	FA (g)	GBFS (g)	H_3BO_3 (g)
MKPC	132.3	262.8	96	-	-	9.8
FA/MKPC	77.8	154.6	96	165	-	6.6
GBFS/MKPC	77.8	154.6	96	-	165	6.6

Table 3.3: Formulations of MKPC based on 0.24 W/S ratio (Gardner, et al., 2015).

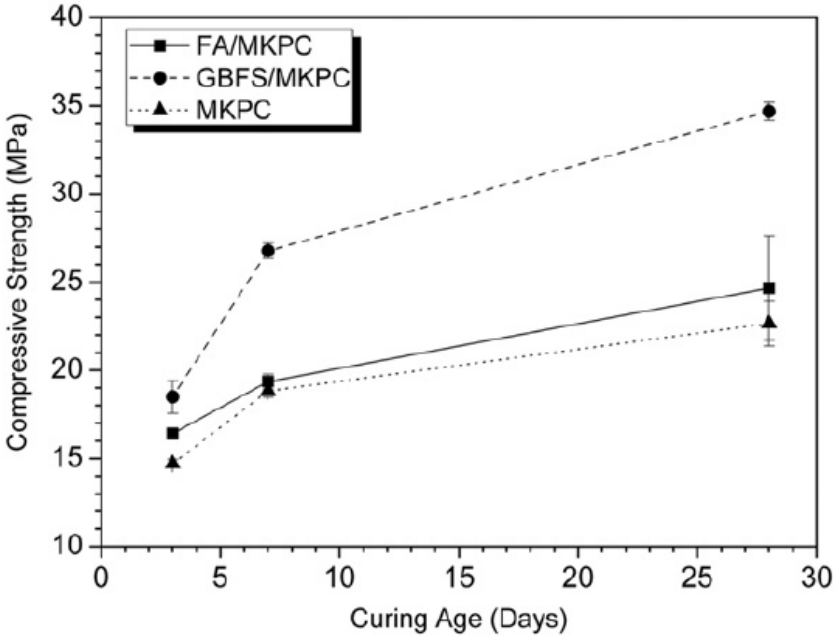

Figure 3.3: Compressive strength development of MKPC, GBFS/MKPC and FA/MKPC (Gardner, et al., 2015).

In some studies, it was suggested that raw materials could be mixed with seawater to form a MKPC without any significant reduction in the compressive strength. For example, Wagh reported that saline water does not deteriorate this type of cement (Wagh, 2016). For this reason, these cements were proposed to be used in marine concrete industry because of the ability to mix with seawater (Mouring, et al., 2003). However, some researchers have investigated the effects of seawater on the properties of these

cements because using seawater might have negative effects on the hardened concrete structure. Their findings have indicated that seawater mixing significantly decreased the strength of MKPC. Importantly, they observed KCI crystals without cementitious properties in the microstructure. It was suggested to be the main reason to explain the decrease in compressive strength that some potassium ions were consumed by chloride ions and less K-struvite was formed. Moreover, it was also reported that the immersion in seawater for 180 days showed deterioration in MKPC samples because of the dissolution of the KCI crystals (Yu, et al., 2017).

On the other hand, addition of mineral admixtures such as silica fume and/or limestone powders in the cement paste eliminated the negative effects of seawater on compressive strength and resulted in a denser cement paste. The positive effect of these fillers was attributed to filling effect and increase of reaction rate by calcium ions (Yu, et al., 2017).

Some researchers studied the use of a low-grade magnesium oxide (LG-MgO) to overcome the economic limitations with the aim of finding a repair cement mortar formulation that shows good mechanical performance and good hardening time (Formosa, et al., 2012). Table 3.4 shows the cement compositions where LG refers to low-grade magnesium oxide and H represents the amount of boric acid in the composition. The results indicated good adhesion strengths (>2 MPa strength). The samples with those formulations were also subjected to durability tests, and they showed good physical properties. It was also reported that samples with lowest boric acid showed the lowest mass loss (Formosa, et al., 2015).

In another study, magnesium phosphate based porous materials with zinc powder additions were investigated to use as fireproofing doors and high temperature furnace insulating lining. The results indicated that increasing zinc content in composition

resulted in longer setting time, higher viscosity, lower hydration temperature, and lower mechanical strength (Fu, et al., 2016).

SETTING TIME

Most of the studies found in the literature show typically less than an hour setting time for these cements. In fact, setting time of cement is critically important for bulk volume applications requiring a few hours to mix the slurry, deliver, pump or place the cement paste, thus setting time should be further controlled (Park, et al., 2016). To better understand the setting time and parameters affecting the setting time myriad experiments have been conducted.

It was reported that such systems might set within 20 minutes without retarders (Lu, et al., 2008; Gardner, et al., 2015). For this reason, retarders such as borax or boric acid (H_3BO_3, 2-3 wt. % of the binder) should be added into the system to control setting time and limit the temperature rise (Lahalle, et al., 2016). Because of little working time, addition of low reactivity magnesium oxide (dead burnt) and supplementary cementitious materials have also been reported to extend the setting time (Soudée & Péra, 2002; Covill, et al., 2011).

According to Wagh, potassium phosphate ceramics can be produced in large amounts with least amount of heat generation because of their highest pH among other acid phosphates while the ceramics formed by ammonium or aluminum hydrogen phosphates can only be produced in small volumes typically less than a gallon (Wagh, 2016). However, it is a significant challenge to produce large volumes of MKPC cements with enough thickening time and desired mechanical properties.

Xu et al. has reported that the M/P ratio has a crucial impact on the rate of hydration where lower M/P ratio leads to faster reaction and higher heat of hydration

(Xu, et al., 2015). Park found the setting time ranging from 15 to 35 minutes depending on the M/P ratio and borax to magnesium (B/M) ratio for the given compositions in Table 3.1. In a similar manner, Hou also investigated the setting behavior and his results indicated a setting time range of 20 to 45 minutes for the given compositions in Table 3.2. The setting time for different M/P ratios is illustrated in Figures 3.4 and 3.5. Studies indicated that an increase in M/P ratio extends the setting time (Park, et al., 2016), but the setting process is still very fast and finishes in less than 45 minutes even with a 5% borax addition (Hou, et al., 2016). It was reported that increasing magnesium content increases the pH of the slurry and accelerates of acid-base reaction (Hou, et al., 2016). According to Park, addition of borax up to 0.08 B/M ratios can improve the setting time, but setting time was adversely reduced beyond 0.08 B/M ratios. Thus, care should be given to borax content in the cement. Additionally, the purity of the magnesium oxide plays an important role and fastens the rate of reaction (Park, et al., 2016).

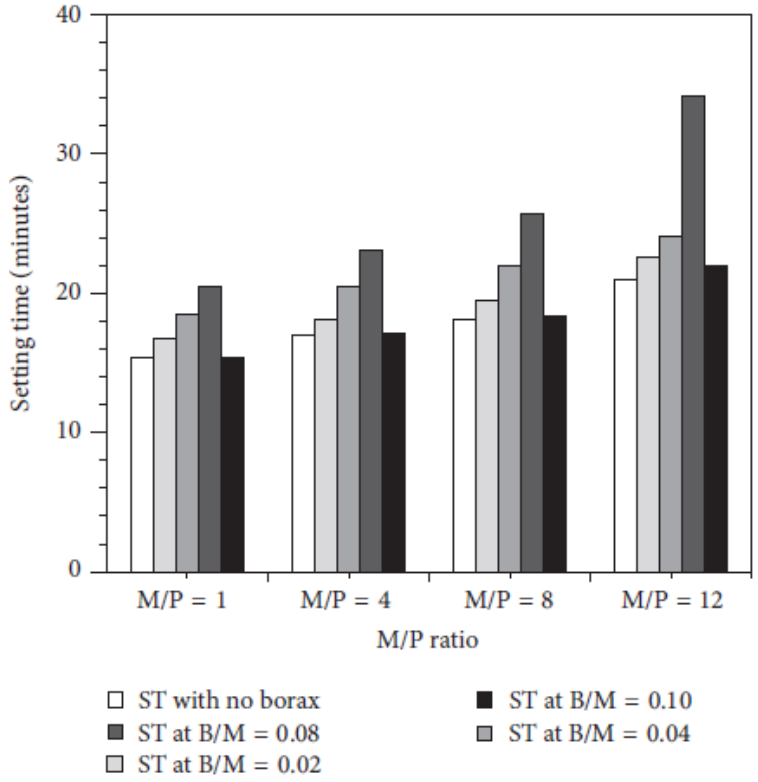

Figure 3.4: Setting time for various M/P ratios and B/M ratios (Park, et al., 2016).

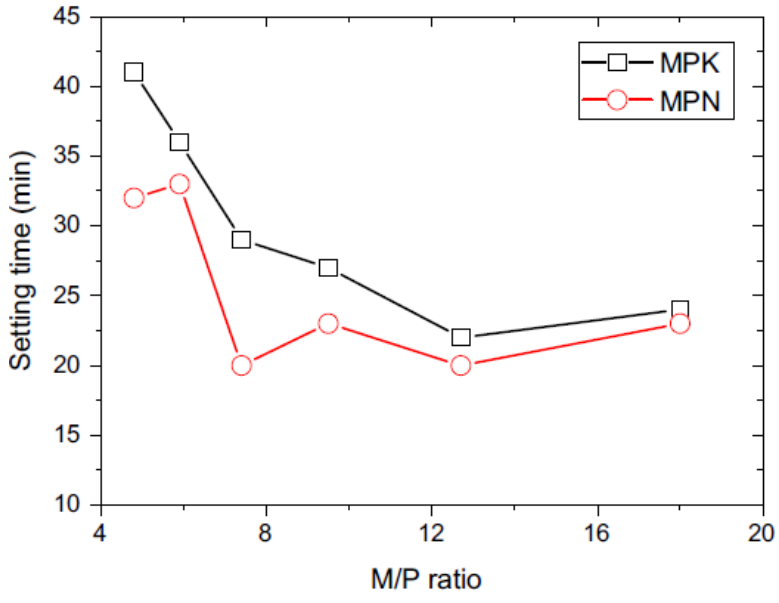

Figure 3.5: Setting time for various M/P ratios (Hou, et al., 2016).

Effects of boric acid on retardation of the MKPC have long been investigated (Lahalle, et al., 2016). Other efforts to increase the setting time have been partial replacement of composition by fly ash, granulated blast furnace slag, aluminate cement (Li & Chen, 2013; Gardner, et al., 2015; Lahalle, et al., 2016) or replacement of water with seawater/saline water (Yu, et al., 2017). However, the effects of seawater have elicited controversial indications by various authors. It was reported that seawater extends the setting time of MKPC since pH of the seawater is higher than fresh water, which helps to slow down the dissolution rate of magnesium oxide particles (Yu, et al., 2017) and improves the fluidity (Yang, et al., 2013). It was also supported by Wagh that saline water retards the setting time (Wagh, 2016). On the other hand, Andrade and Schuiling proposed that higher pH environment could contribute the precipitation and crystallization (Andrade & Schuiling, 2001).

There has also been an investigation of magnesium phosphate based porous materials for fireproofing doors and high temperature furnace insulating lining by means of a chemical foaming process using zinc powders. The results indicated that a longer setting time can be obtained with increasing zinc content (Fu, et al., 2016).

MICROSTRUCTURE

The microstructure of MKPC samples has been investigated by different techniques such as SEM, XRD, and TEM. In general, a highly dense and crystalline microstructure is observed. Microstructure consists of mostly K-struvite minerals and some amount of unreacted magnesium oxide grains. In this section, findings from different authors will be provided.

Lahalle et al. demonstrated the mineralogical evolution of MKPC systems and phase transformations leading to precipitation of K-struvite. Since the dissolution of

$Mg_2KH(PO_4)_2*15H_2O$ is delayed, the precipitation of K-struvite is delayed with increasing boric acid. Thus, it was reported that the precipitation of the hydrates was retarded either directly or indirectly by stabilizing the magnesium in the solution by boric acid addition. Increasing boric acid in the slurry alters the microstructure of the final hydration product while favoring precipitation of more cattiite against K-struvite crystals. It was observed that final mineralogical structure consisted of 81% K-struvite and 19% cattiite (Lahalle, et al., 2016).

In another study, larger K-struvite crystals were observed in microstructure with specimens prepared using boric acid. It was attributed that slower reaction rate allows more time for crystal growth within the sample. On the other hand, a highly dense crystalline structure was observed in FA/MKPC specimens where large K-struvite crystals were surrounded by fly ash cenospheres. XRD and TEM images showed coexistence of both crystalline and amorphous phases in the hydration products, where crystal structure was identified as periclase and struvite (Park, et al., 2016). It is necessary to note that magnesium oxide minerals form periclase minerals when calcined at very high temperatures. It was suggested that the coexistence of different phases helps the strength development, and denser the microstructure, the higher the performance of the cement (Ding, et al., 2012).

Back Scattered Electron Images of FA/MKPC and GBFS/MKPC systems are shown in Figure 3.6. The formation of a continuous K-struvite phase is common in both GBFS/MKPC. According to XRD, SEM and TEM analysis, a polycrystalline structure containing mostly struvite and unreacted magnesia exist in the microstructure where residual magnesia grains are fine aggregates in the hardened matrix. In addition, it was reported that finer magnesia grains produce denser microstructure, which increases the performance and the strength of the material (Ding, et al., 2012).

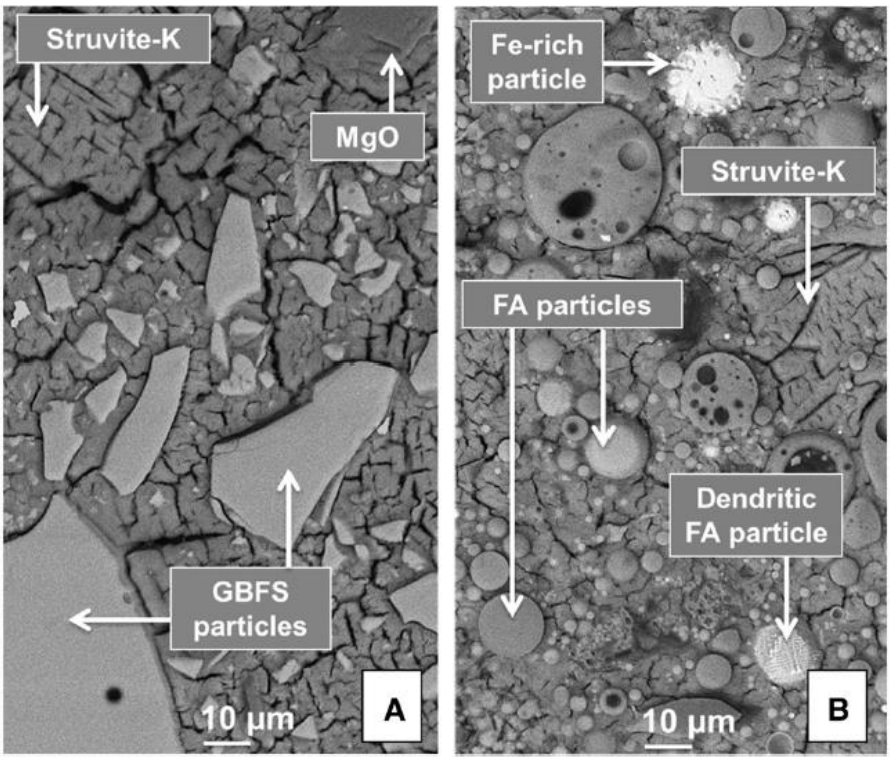

Figure 3.6: Back Scattered Electron Micrographs of a) GBFS/MKPC b) FA/MKPC after 28 days of curing (Gardner, et al., 2015).

In another study, it was proposed that a dense matrix with high mechanical strength, impermeable to water can be obtained when glassy aluminosilicate fraction of fly ash reacts in the acidic MKPC solution while forming a secondary phase except from K-struvite (Ding & Li, 2005; Xing, et al., 2011). Gardner et al. have characterized the assemblage of the MKPC blended with fly ash or blast furnace slag. Microstructural characterization and multinuclear NMR spectra indicated that dissolution of glassy aluminosilicate fractions was dominant in the MKPC binder, and in addition to main K-struvite phase, potassium aluminosilicate phase was observed. It was proposed that

additional phases formed through new chemical reactions in FA/MKPC systems might enhance the density and durability of the cement (Gardner, et al., 2015).

EVOLUTION OF pH AND ELECTRICAL PROPERTIES

Many researchers demonstrated the pH evolution with and without boric acid addition. Previous studies have reported stabilized pH values around 7-8 (Wagh, et al., 1999). It was also reported that struvite is a stable phase over a large pH range from 7.0 to 10.0 (Andrade & Schuiling, 2001). In an attempt to develop a low pH magnesium potassium phosphate cement to facilitate the biodegradation in combination with stabilization/solidification processes, researchers reported that stabilized pH of the system was in the range of 6-9.5 for magnesia to phosphate ratios of 1-1.5 (Iyengar & Al-Tabbaa, 2007). In the absence of boric acid, it was observed that the pH of the slurry increased from 4.3 to 10.4 during the test. The pH was found to be 8.8 after 32 hours for system number 5. Thus, increasing boric acid concentration reduced the final pH of the material. Table 3.4 shows the composition of 5 different systems. According to Table 3.4, the only variable is the boric acid with increasing concentration from system #1 to system #5. Figure 3.7b shows the influence of boric acid concentration on the evolution of pH. In general, pH of the acidic solution is around 4, and pH rises and stabilizes around 8 after the reaction is complete (Lahalle, et al., 2016).

Roy reported that these cements have potential in electronic packaging because certain cements were found to be nonconductive with low dielectric permittivity and losses (Roy, 1987). According to Figure 3.7a, increasing boric acid concentration retards the reaction and leads to higher residual electrical conductivity at the end of the experiment (Lahalle, et al., 2016).

System #	W/C wt.	Mg/P ratio	MgO (g)	KH_2PO_4 (g)	H_3BO_3 (g)	$[H_3BO_3]$ mmol/L	H_3BO_3/C (wt.%)
#1	100	1	0.57	1.93	0	0	0
#2	100	1	0.0645	1.93	0.0645	4.17	2.58
#3	100	1	0.154	1.93	0.154	10	6.16
#4	100	1	0.309	1.93	0.309	20	12.36
#5	100	1	0.645	1.93	0.645	41.7	25.8

Table 3.4: Composition of the MKPC Systems (Lahalle, et al., 2016).

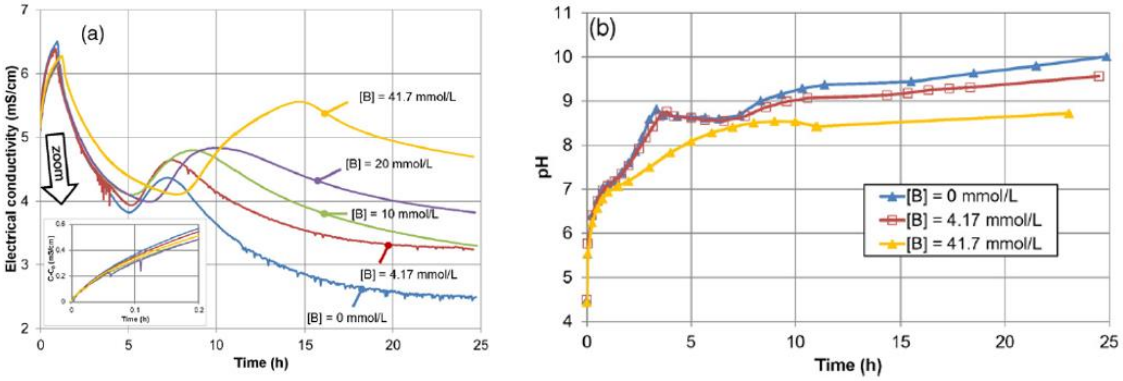

Figure 3.7: a) Electrical conductivity evolution b) pH over time (Lahalle, et al., 2016).

POROSITY AND PERMEABILITY

Wagh reported that ceramics exhibit a dense structure with < 1% porosity, but most Portland cements show typically a porosity of 15-20% (Wagh, 2016). Therefore, it was expected to observe porosity values in between ceramics and Portland cements. However, a wide range of porosity values was observed in the literature due to the variety of compositions and formulations. It was proposed that experimental procedure, curing conditions and impurities present in the magnesia can affect the porosity and permeability of cement (Iyengar & Al-Tabbaa, 2007). It was also previously reported that removal of

entrapped air can help the formation of a denser, less porous structure by applying modest pressures (up to 5MPa) (Roy, 1987).

It was observed that porosity of the samples increased with increasing boric acid concentration and M/P ratio. It was shown that an increase in M/P ratio resulted in more pore volume. The porosity of the MKPC samples ranged from 13.9% to 25.5% and Portland cement samples ranged from 17% to 21% by mercury intrusion test (Park, et al., 2016). Similarly, in another study where a low-grade magnesium oxide byproduct was used in the experiments, a range of porosity from 12.5% to 28.8% was observed with increasing boric acid content (Formosa, et al., 2015). Moreover, the samples prepared with seawater were found to be more porous than the samples with fresh water. Also, it was reported that samples with silica fume and limestone powders demonstrated less porosity (Yu, et al., 2017).

Interestingly, Ceramicrete samples developed by Argonne National Laboratory showed low porosity (0.3% volume) and low permeability (0.004md water permeability) (Wagh, et al., 2005). Properties of the materials can be seen in Table 3.6. A volumetric expansion of 1.57 % to 2.61 % was reported, and it was attributed to the air entrapped in the samples during rapid hardening (Wagh, 2016).

BONDING CHARACTERISTICS

The MKPC cements were reported to have excellent bonding characteristics to many materials such as steel, cold joint bonding, wood (cellulose materials) and other earth materials (sandstone and limestone). However, it was reported to have poor bonding characteristics to dolomite and it does not adhere to plastic (Wagh, 2016).

VISCOSITY AND INJECTION CHARACTERISTICS

A study focusing on viscosity and injection characteristics of these cements reported that low viscosity/pump-easy cements can be prepared by decreasing the powder to liquid ratio (Khairoun, et al., 1998); however, increase in the water may have detrimental effects on cement microstructure by forming a more porous structure (Ishikawa & Asaoka, 1995). Chemicals to improve the ability for injection were reported as lactic acid, glycerol, chitosan, citric acid or soluble polymers (Leroux, et al., 1999; Ginebra, et al., 2001). Modifications to composition can alter the properties of the cements. For example, Wagh and his coworkers developed low viscosity pump-easy chemically bonded phosphate cement pastes, which set underwater (even seawater) (Wagh, 2016).

FORMULATIONS PROPOSED AS WELLBORE SEALANTS

In the literature, one of the potential applications of chemically bonded phosphate cements can be observed as borehole sealants in the oil and gas industry. The wells in arctic regions or the wells in geothermal fields demand critical mechanical properties on cements. For this reason, many CBPC formulations have been investigated as borehole sealants for wells at arctic regions and/or geothermal fields.

For high temperature geothermal wells; alumina, ammonium phosphate, sodium metaphosphate, fly ash and calcium aluminate mixtures have been formulated to develop CBPC (Sugama, 1996). Research on aging properties predicted the durability of these cements to be up to 20 years in downhole environment conditions (Sugamo & Carciello, 1993). Later, all the research led to the development of a CBPC cement, namely ‘Thermalock’ for geothermal wells by Halliburton Energy Services and Unocal Corporation in collaboration with Brookhaven National Laboratory. Thermalock has been

successfully applied in the geothermal wells and it has been reported as the only field application of CBPC as a borehole sealant in the literature (Wagh, 2016).

For arctic/permafrost wells, water in the cement slurry should not freeze until the cement sets (Cameron, et al., 1971). Moreover, cement should not disturb the ice network around the wellbore to prevent thawing of near wellbore region and to avoid well integrity problems in the future. Therefore, significant research for cement formulations has been conducted for successful cementing operations in arctic regions. The freeze temperature depressants such as salts, alcohol, and polymers are commonly used to lower the freezing point of water so that cement can set even at subzero temperatures. However, they should be carefully used because excess amounts can lower the ultimate compressive strength and cause well integrity problems (Limaye, et al., 2011). Up to now, cements with high proportions of calcium aluminate have been used successfully in Canada and Alaska North Slope since they can set at low temperatures; however, it is also found that Portland cement contamination can lead to abrupt setting of these cement systems (Maier, et al., 1971).

Argonne National Laboratory (ANL) focused on developing CBPC for a wide range of downhole temperatures and pressures and proposed a formulation for permafrost and shallow wells. The formulation developed by ANL was named as Ceramicrete, blended with wollastonite and fly ash. It has been reported to achieve a low thermal conductivity (0.27w/mK), low heat generation, high thaw resistance and good sealing properties with effective prevention of gas migration. It has also been reported to employ a low drying shrinkage (Qiao, et al., 2010) and good bonding characteristics to steel, cold joint bonding, wood (cellulose materials), sandstone and limestone, but poor bonding characteristics to dolomite and plastic (Wagh, 2016). In addition, it exhibits low porosity (0.3% volume), low permeability (0.004md water permeability), up to 5 hours of

thickening time and high compressive strength (Wagh, et al., 2005). Owing to positive laboratory results, it was approved for further field-testing at BJ Services yard in Texas in 2006. Later, Ceramicrete formulations with and without Portland cement contamination have also been tested and showed positive results. A new formulation with thickening time of 5 hours and a lower heat generation has been proposed (Hemsath, et al., 2007). It has also been reported to have a low viscosity, set rapidly (even underwater) and achieve compressive strengths in a range of 55MPa to 83MPa (Wagh, 2016). The compositions of the Ceramicrete formulations are provided in Table 3.5, and a comparison with Portland cement is given in Table 3.6. Despite the proposed formulations, no field-testing has been reported through 2006 to 2010 (BP, et al., 2011). ANL reported that pumping the cement components separately and mixing them on the way to annulus can allow in situ reaction and setting. Findings also indicated that temperature, which affects the reaction rate and solubility of metal oxides remarkably, is the only key parameter to consider formulating a CBPC and pressure has negligible effects.

MgO	KH_2PO_4	Fly Ash	Thickening Time	Remarks
10	30	60	N/A	Water in the slurry frozen, not set
12.5	37.5	50	>5 hr	Cement set well after 5 days
15	45	40	>5 hr	Cement set well after 5 days
37.5	37.5	25	3hr 25min	Slurry hardened within 4hr at 30ºF
35	37.5	27.5	5hr 45min	Ash was replaced by wollastonite

Table 3.5: Various Ceramicrete compositions with 0.5 wt.% boric acid in powder compositions in all cases. (Wagh, et al., 2005).

Property	Cement		Remarks
	Phosphate	Portland	
Density (g/cm3)	1.7-1.9	2.4	CBS is lighter
Slurry density (g/cm3)	1.5-1.7	1.8	CBS slurry is lighter and easier to pump
Open porosity (vol.%)	0.3	≈5	No pore fluids in CBS; therefore, stable in freeze-thaw cycles
Permeability (md)	0.004	≈0.1	CBS is impermeable
Room temperature compressive strength (psi)	7000-8000	≈4000	High strength of CBS allows addition of cenospheres, etc., that improve thermal properties and reduce slurry weight
Thermal conductivity (W/m K)	0.27	0.53	CBS is a better insulator
Heat of fusion (J/cm3)	347	514-640	Low heat of fusion ensures less thawing of permafrost region during CBS setting
Setting in hydrocarbon environment	Unaffected by CO2	Flash sets by carbonation	CBS is most useful in gas hydrate regions

Table 3.6: Comparison of Ceramicrete and Portland Cement (Wagh, 2016).

Limaye et al. has also investigated the Ceramicrete formulations to compare its performance with Portland cement as oil field cements in arctic regions. He has prepared Ceramicrete samples at 4.4ºC, 10ºC, and 21.1ºC and cured them at 0ºC for 24 hours to simulate the arctic conditions. According to his results, magnesium oxide is an expansive additive, and the optimum amount of it should be present in the composition to prevent crack development (Limaye, et al., 2011). In another study, a volumetric expansion of 1.57% to 2.61% was also reported for shallow to deep wells respectively during Ceramicrete formulations, and volumetric expansion was attributed to entrapped air in the samples during rapid hardening (Wagh, 2016). It has been reported that the higher or lower amounts of MgO can lead to crack development. The expansion tests at 4.4ºC resulted in the development of cracks. The study also reported that the strength of the cement depends on the water ratio and contamination with Portland cement (5% contamination with G grade California Portland cement) indicated no alteration in compressive strength. In his study, it has been reported that Ceramicrete formulations by Argonne National Laboratory flash sets with 5% Portland cement contamination. Moreover, the heat evolution causes thawing the permafrost and well integrity problems. The formulations studied by Limaye et al. are provided in Table 3.7. Among the formulations given in Table 3.7, the formulation for sample #1 has been proposed as a suitable option for safe and economic completion operations in arctic wells in Alaska North Slope without crack development and less fluid loss than other formulations (Limaye, et al., 2011). In general, the performance of the MKPC compared to Portland cement has indicated positive results, and many different formulations have been proposed for wells in arctic/permafrost regions. However, application of MKPC for permafrost or shallow wells have not been reported yet despite the proposed formulations for the oil and gas industry.

Ceramicrete Formulations by Limaye et al. (Compositions in wt.%)				
Contents	Base	Sample #1	Sample #2	Sample #3
MgO	25	22.9	21.5	19.9
KH_2PO_4	27.2	28.5	29.1	30.1
C-class fly ash	10.21	10.6	11	11.3
Wollastonite	10.2	10.6	11	11.3
Boric acid	0.09	0.1	0.1	0.1
Water	27.3	27.3	27.3	27.3
Total	100	100	100	100

Table 3.7: Formulations of Ceramicrete binder (Limaye, et al., 2011).

Chapter 4: Experimental Analysis

This chapter describes experimental analysis conducted by this study. It introduces the raw materials utilized in the experiments, briefly explains cement slurry preparation, and test methods to measure the mechanical properties. All laboratory experiments in this section have been conducted at 72 ºF temperature and under atmospheric pressure conditions unless otherwise stated. Magnesium oxide (MgO), potassium dihydrogen phosphate (KH_2PO_4) and fly ash powders are mixed homogeneously at a fixed ratio of M/P 1:3 and a ratio of M/FA 1:4. Retarders such as boric acid, borax, salt, HR4, and HR5 have been added in the slurry to improve thickening time. Thinners such as potassium lignite (K-Lig), Q-Broxin (a dispersant and filtration control agent), and carbonax (an unmodified lignite) have also been employed in some experiments in an attempt to reduce the viscosity of the slurry for easy pumping considerations.

RAW MATERIALS

Magnesium oxide powder was obtained from Fisher Scientific Company (M68-500 Heavy Powder, Purity Grade: USP/FCC; M300-500 Purity Grade: Electronic; M68-3 Heavy Powder, Purity Grade: FCC/USP) and from Sigma Aldrich Company (≥99% trace metals basis, -325 mesh, PN: 342793, CAS: 1309-48-4). Since the reactivity of the magnesium oxide plays a crucial role in reaction rates, the grade of the magnesium oxide is specifically stated in this study where necessary. Potassium dihydrogen phosphate powder was obtained from Acros Organics and Ward's Science companies (Assay: >99%, ACS reagent grade, CAS: 7778-77-0). Boric acid was obtained from VWR International BDH chemicals. Halliburton provided HR4 and HR5 cement retarders. Finally, Class C and Class F fly ash powders were obtained from Charah Solutions Inc.

PREPARATION OF CEMENT SLURRY

The magnesium potassium phosphate cement samples were prepared by mixing 12.5 wt. % magnesium oxide (MgO), 37.5 wt. % potassium dihydrogen phosphate (KH_2PO_4) and 50 wt. % fly ash. After measuring the weight of the dry powders, all dry powders were mixed homogeneously. Additives such as boric acid, borax, salt, Halliburton cement retarders (HR4 & HR5), and a variety of thinners were also employed in the composition of the cement slurry to investigate the effects of these chemicals on thickening time and compressive strength. The additives and tap water were mixed before adding raw materials (dry powder mixture), and the cement slurry was mixed and prepared according to API 10A specifications. Then, cement slurry was poured into 2-inch cubic plastic molds. One of the plastic molds was always used for measuring the thickening time via a magnetic stirrer, and the other molds were left undisturbed and cured at 72 ºF under atmospheric pressure for 24 hours. Finally, the samples were crushed to measure the compressive strength.

TEST METHODS

Initially, cement slurries having different compositions were observed physically for thickening time and compressive strength development after 24 hours. Then, compositions with the longest thickening time and enough compressive strengths were chosen for further testing.

Thickening time of cement slurry is measured by a device called as consistometer, where the consistency of the slurry is measured as a function of nonlinear viscosity of the slurry. The consistometer allows application of high pressures and temperatures on the cement slurry while the slurry is constantly mixed at 150 rpm. In this manner, 70Bc -

Bearden Consistency unit is regarded as the thickening time of the cement slurry, and 100Bc refers to fully set cement according to API standards.

Determination of the thickening time can also be achieved with high accuracy by using a magnetic stirrer. In fact, thickening time data from a consistometer can be closely replicated/reproduced by arranging revolution per minute (rpm) setting of a magnetic stirrer. For this reason, a consistometer test was run with a candidate composition, and then thickening time results were replicated with the magnetic stirrer. As a result, thickening time data in this study has been determined by using magnetic stirrers. Finally, a destructive compressive strength tester has been utilized to measure the compressive strength of samples after curing cement samples at 72 ºF temperature and under atmospheric pressure for 24 hours.

Chapter 5: Results and Discussions

This chapter presents the experimental results and discussions. Critical results and unexpected findings from the experiments are documented in five different sections to evaluate the results in a more organized manner. Temperature evolution and right angle set behavior, effects of additives on mechanical properties, and overall thickening time and compressive strength results are provided. In addition, a cost analysis is also conducted by available raw material prices, and additional notes are provided at the end of this chapter.

TEMPERATURE EVOLUTION AND RIGHT-ANGLE SET BEHAVIOR

Initially, several cement slurries were prepared with different compositions and physically observed for thickening time. Thickening time of the slurry having the composition given in Table 5.1 was estimated to be around 2:30 hours. Also, the compressive strength at 24 hours has been measured in the range of 500-700 psi. Thus, it was selected for further testing, and a consistometer test was run to determine actual thickening time. The temperature was set to 80 ºF, the pressure was set to 1000 psi (lowest) and increase to 2000 psi in 30 minutes. Surprisingly, initial temperature of the cement slurry has been recorded as 113.5 ºF. Since the temperature was set to 80 ºF, it has gradually dropped to 80 ºF. In addition, initial Bc has been recorded as 112 Bc, which was already greater than 100 Bc implying a fully set cement, high viscosity, and gel strength. Then, consistency has decreased to 70.8 Bc in 2 minutes and achieved a minimum of 52 Bc. More importantly, the trend for the consistency has shown a sharp rise from 72 Bc at 1:14 hours to 88 Bc in 2 minutes. Then, test was terminated. The trend for consistency and temperature profile is provided in Figure 5.1. Thickening time of the slurry has been recorded as 1:24 hours considering the time for preparation, mixing and

placing the slurry in the consistometer. Also, the compressive strength of samples has been found in the range of 625 psi to 675 psi after destructive crash tests.

Sample	MgO	KH_2PO_4	F Class Fly Ash	Additives		Water	Thickening Time	Compressive Strength
				Boric Acid	Salt			
#	(g)	(g)	(g)	(g)	(g)	(g)	(hr:min)	(psi)
1	12.5	37.5	50.0	3.0	3.0	38.5	2:30	500-700

Table 5.1: Composition of the candidate sample and physical observations.

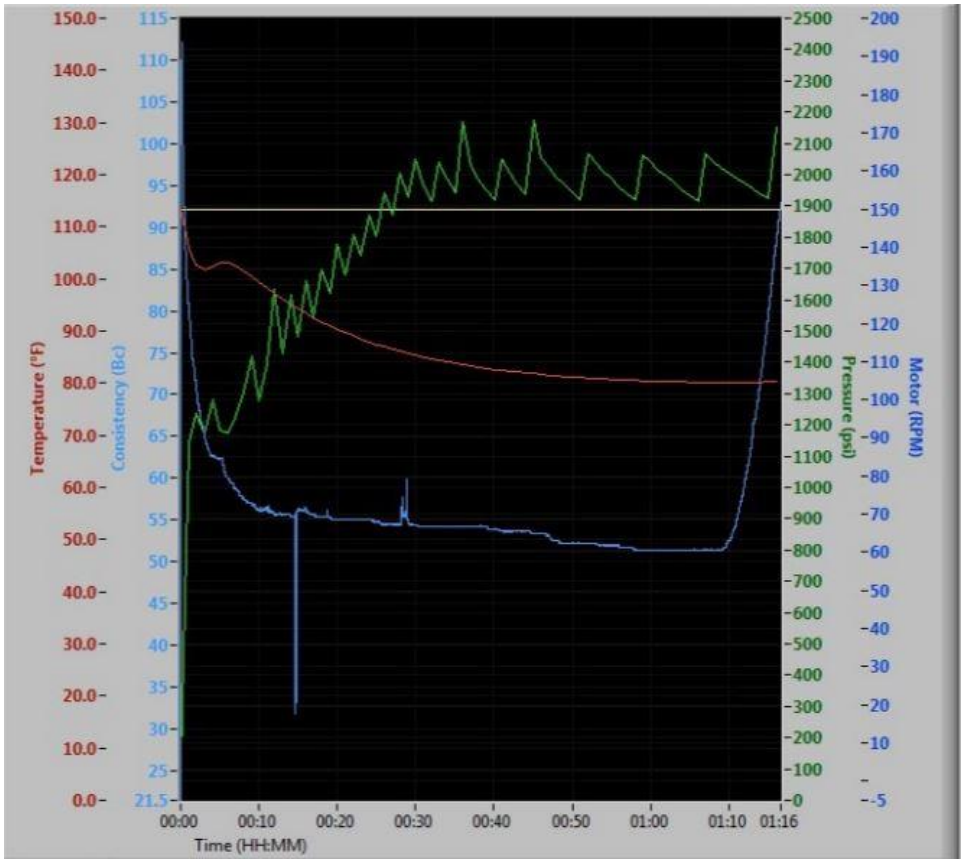

Figure 5.1: Consistometer test results of candidate composition.

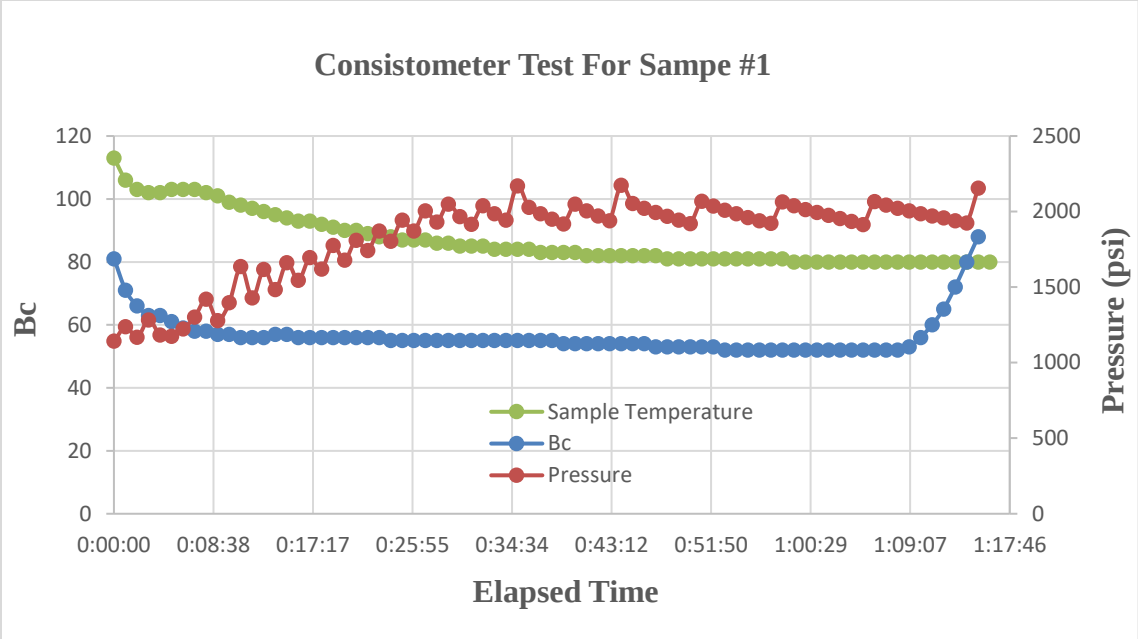

Figure 5.2: Bearden consistency unit evolution over time for candidate composition.

The result of the consistometer test clearly indicates that these cements generate considerable amounts of heat and exhibit a rapid hardening with a right angle set behavior. The grade/reactivity of the magnesium oxide is also closely related to the heat of formation, and the reaction rate is accelerated with increasing reactivity of magnesium oxide. The tested slurry was prepared by using M300-500 grade magnesium oxide. In fact, relatively hotter molds have been observed with M300-500 grade compared to M68-3 heavy powder grade magnesium oxide. As can be seen from Figure 5.1 and Figure 5.2, a dramatic temperature rise was recorded as 113.5 ºF while the slurry was prepared at 72 ºF. Furthermore, the temperature was cooled down to 80 ºF because of the consistometer temperature setting. Ultimately, such a temperature rise can be a problem for permafrost to shallow wells, and it is certainly questionable without performing conductivity tests. Therefore, further tests are required to analyze the temperature evolution and thermal conductivity of the cement slurry with given composition.

A right angle set behavior indicating a rapid hardening process is a desirable property for many cementing applications. However, thickening time of nearly 1:30 hours is still not enough for bulk volume cementing operations in the oil and gas industry. The sudden rise in the Bearden consistency units shown in Figure 5.1 and Figure 5.2 clearly exhibits a rapid hardening property.

The slurry was also mixed at different rates by using a magnetic stirrer to reproduce the thickening time data from the consistometer. The results are provided in Table 5.2 where thickening times of 4:30 hours at 350 rpm, 1:55 hours at 250 rpm, and 1:30 hours at 150 rpm were recorded by the magnetic stirrer, which is 1:24 hours by the consistometer. Thus, it is possible to replicate the consistometer data for thickening time by arranging the rpm setting of a magnetic stirrer.

MgO	KH_2PO_4	F Class Fly Ash	Additives		Water	Thickening Time	Remarks
			Boric Acid	Salt			
(g)	(g)	(g)	(g)	(g)	(g)	(hr:min)	(rpm)
12.5	37.5	50.0	3.0	3.0	38.5	2:30	Physical observations
						4:30	350rpm Magnetic stir.
						1:55	250rpm Magnetic stir.
						1:30	150rpm Magnetic stir.
						1:24	150rpm Consistometer

Table 5.2: Thickening time results with magnetic stirrer and consistometer.

In general, MKPC exhibit a thixotropic behavior (shear thinning property). They demonstrate high viscosity and gel strength in static motion and become less viscous under shear. The Bc trend in Figure 5.1 and thickening time data in Table 5.2 confirm the

thixotropic behavior. However, the less pumpable a cement slurry is, the more force/power is required to pump/place. For this reason, thinners were added in slurry composition in an attempt to increase the fluidity and the ability to pump easily, but they did not improve fluidity/viscosity of the cement slurry. Further information related to thinners can be found in the additional notes on the experiments section.

EFFECT OF SALT ON THICKENING TIME AND COMPRESSIVE STRENGTH

Salt was added to cement slurry in various proportions to improve thickening time. Indeed, salt addition causes a delay in the reaction rate and increases the thickening time of the slurry. However, it reduces the overall compressive strength of the samples. For example, samples with 2.5 wt. % boric acid have achieved a thickening time of 1:15 hours and compressive strengths around 1000 psi. Thickening time has been greatly improved to 2:44 hours with 1 wt. % salt addition, but compressive strengths have fallen below 1000 psi. The compositions, which employ various quantities of salt, are summarized in Table 5.3.

In another set of experiment, thickening time of the slurry has been extended from 1:35 hours to 3:27 hours for the given composition with 3 wt. % boric acid and 1 wt. % salt addition. In an extreme case, i.e. up to 4 wt. % salt in the composition achieves more than 8 hours thickening time. However, excess salt in composition remarkably deteriorates the compressive strength development. Overall, optimum amounts of salt should be employed in the composition, and a maximum of 1 wt. % salt addition is found to be acceptable to maintain compressive strengths above 500 psi in this study.

THICKENING TIME AND COMPRESSIVE STRENGTH RESULTS

Depending on the type of additives and their amounts in the composition, a wide range of thickening time and compressive strength values can be obtained for MKPC. In the scope of this study, a fixed ratio of 1:3 magnesium oxide to potassium phosphate has been utilized, and the effects of additives on thickening time and compressive strength have been investigated. All formulations and resulting thickening time and compressive strength values are presented in Table 5.3. It is necessary to say that the compositions in Table 5.3 contain M68-3 heavy powder grade magnesium oxide and ACS reagent grade potassium phosphate. The results are also graphically presented in Figure 5.3. Unfortunately, only a few formulations demonstrated sufficiently long thickening times greater than two hours and compressive strengths greater than 500 psi. However, well cementing operations requiring small volumes can still take place conveniently with less than two hours thickening time. Figure 5.4 selectively depicts the MKPC formulations suitable for oil and gas industry fulfilling the thickening time and compressive strength requirements.

Among the cement formulations in Table 5.3, the formulation with 3 wt. % boric acid and 1 wt. % salt achieves by far the longest thickening time of 3:27 hours and compressive strengths around 750 psi. The formulation with 2.5 wt. % boric acid and 1 wt. % salt demonstrates 2:44 hours of thickening time, the one with 5 wt. % boric acid shows about 2:40 hours of thickening time, and finally the formulation with 4 wt. % boric acid yields 2:30 hours of thickening time and compressive strengths around 500 psi. These formulations are demonstrated in Figure 5.4. Consequently, they achieve more than two hours of thickening time and more than 500 psi compressive strength under the given temperature and pressure conditions.

Compressive strength highly depends on the composition of the cement. Excess boric acid and/or salt in the composition negatively affects the compressive strength development. Among the formulations mentioned above, the formulations including 2.5 wt. % boric acid yield highest compressive strengths ranging from 900 psi to 1200 psi. However, increasing boric acid concentration up to 5 wt. % lowers the compressive strength of samples to 450 psi to 600 psi range slightly yielding the critical 500 psi requirement in compliance with API standards. Further increase in boric acid (>5 wt. %) causes volumetric expansion, crack development (particularly horizontal cracks) and eventually failure in compressive strength. In addition, it has been observed through the experiments that replacement of boric acid with borax slightly improves the compressive strength of the samples (nearly up to 10% of original compressive strength).

HR4 and HR5 Halliburton cement retarders were also added to the slurry to improve the thickening time. However, these additives have been found heterogeneously in crushed samples in all cases. Particularly, a brittle layer of HR4 and/or HR5 has been observed at the surface of the cement slurry, and removal of samples from plastic molds were harder due to brittle top layer; cracking and leading to an uneven surface for compressive strength testing. In other words, the samples cracked easily during the extraction process from plastic molds, and excess HR4 and HR5 have resulted in poor compressive strength. Ultimately, the use of these chemicals is not suggested for MKPC formulations because of crack development, volumetric expansion, and failure in compressive strength.

The experiments in the scope of this study have been conducted by using both class C fly ash and class F fly ash. In general, it has been observed that class C fly ash performs better than class F fly ash in MKPC formulations because the compressive strength of samples with class F fly ash was generally lower than that of class C fly ash.

MgO	KH_2PO_4	Fly Ash		Boric Acid	Salt	HR 4/5	Water	Thickening Time	Compressive Strength
		C	F						
(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(hr:min)	(psi)
12.5	37.5	50	-	2.5	-	-	38.5	1:15	900-1200
12.5	37.5	50	-	3	-	-	38.5	1:35	800-1100
12.5	37.5	50	-	4	-	-	38.5	2:30	525-650
12.5	37.5	50	-	5	-	-	38.5	2:40	450-600
12.5	37.5	50	-	5	-	-	38.5	2:32	475-525
12.5	37.5	50	-	10	-	-	38.5	N/A	250
12.5	37.5	50	-	20	-	-	38.5	N/A	N/A
12.5	37.5	50	-	2.5	1	-	38.5	2:44	800-900
12.5	37.5	50	-	3	1	-	38.5	3:27	725-850
12.5	37.5	50	-	3	2	-	38.5	5:10	250-300
12.5	37.5	50	-	3	4	-	38.5	8:30	0-150
12.5	37.5	50	-	4	1	-	38.5	3:05	250
12.5	37.5	50	-	3	-	3	38.5	1:06	200
12.5	37.5	50	-	3	-	5	38.5	1:24	225
12.5	37.5	-	50	2.5	-	-	38.5	0:43	350-375
12.5	37.5	-	50	5	-	-	38.5	0:45	250
12.5	37.5	-	50	10	-	-	38.5	0:48	200
12.5	37.5	-	50	2.5	1	-	38.5	1:05	275
12.5	37.5	-	50	3	1	-	38.5	1:30	250
12.5	37.5	-	50	3	3	-	38.5	1:50	200
12.5	37.5	-	50	3	-	3	38.5	0:45	200
12.5	37.5	-	50	3	-	5	38.5	0:50	225

Table 5.3: Thickening time & compressive strength results for different compositions.

The results with class F fly ash are shown in Figure 5.5. For instance, while samples with class C fly ash demonstrated nearly 1000 psi compressive strength with 2.5 wt. % boric acid, samples with class F fly ash only exhibited around 375 psi compressive strength. In addition, cracks and volumetric expansion have been more severely observed in samples with class F fly ash. Consequently, all proposed formulations in Figure 5.4 involve C class fly ash in the composition, and C class fly ash is suggested for MKPC formulations.

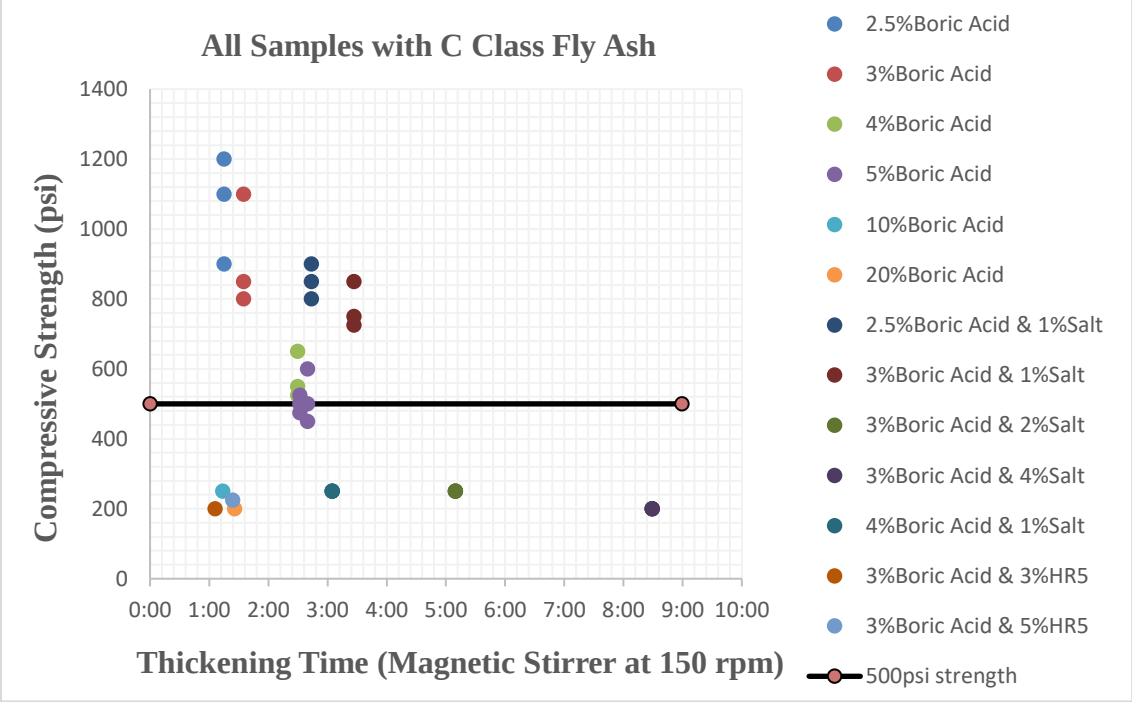

Figure 5.3: Compressive strength vs thickening time results with class C fly ash.

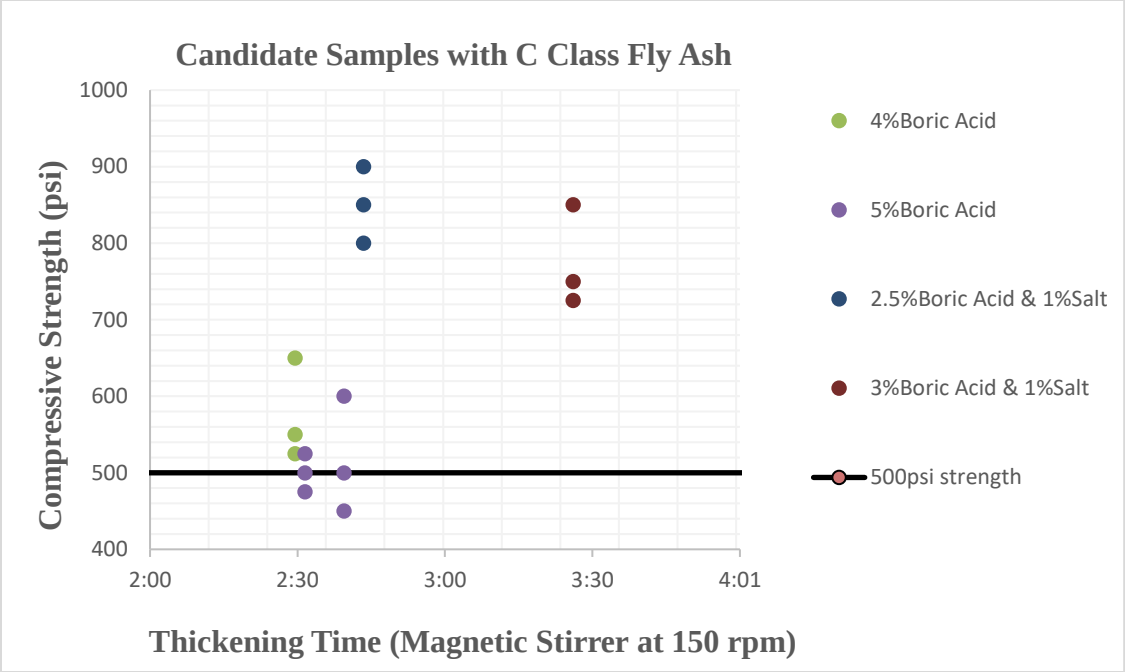

Figure 5.4: Prospective MKPC formulations with more than two hours thickening time.

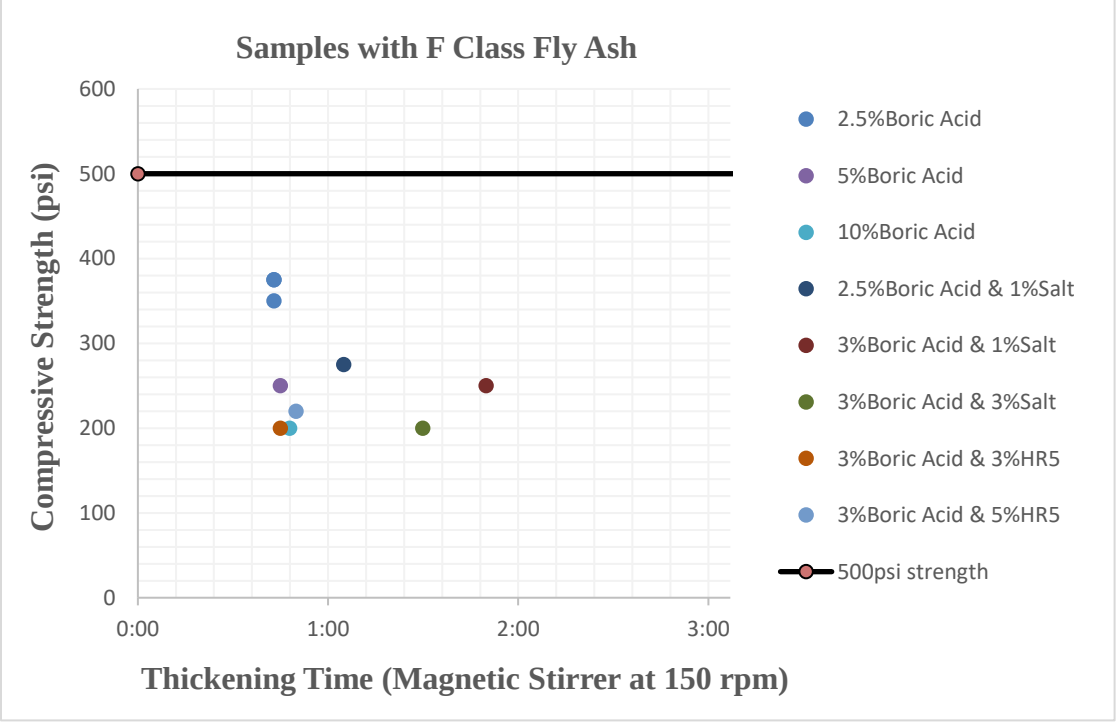

Figure 5.5: Compressive strength vs thickening time results with class F fly ash.

COST ANALYSIS

In the literature, very few authors have mentioned the high cost of raw materials; thereby the cost of these cements. While some authors have claimed that the high cost of raw materials besides the costs associated with calcination process at high temperatures is the main disadvantage for its potential use as a substitute for Portland cement in some applications, some others claimed that these cements can be a substitute for Portland cement. For instance, it was claimed that low cost of these ceramic-cement materials beside excellent mechanical properties, rapid setting, and formation at room temperature makes them viable alternatives to Portland cement in myriad applications (Wagh, 2016). In a previous study, it was stated that Ceramicrete material cost is generally 50% higher than Portland cement and the advantages of this material can offset the costs (Wagh, et al., 1999). Some authors also suggested that use of less expensive byproducts could make these cements more feasible for bulk volume applications (Formosa, et al., 2015). In addition to the cost disadvantage, the main problems limiting their applications were reported to be their rapid hardening process, the heat of hydration, and poor water stability (Yu, et al., 2017).

Although raw material prices can change dramatically from supplier to supplier or buying small or large quantities can make huge differences in pricing, a cost analysis has been conducted by considering average raw material prices available online. According to the average bulk prices seen in Table 5.4 where prices were retrieved from Alibaba.com in April 2018, a price per barrel calculation indicates that these cements are nearly 10 times more expensive than Portland cement. A cost comparison is provided in Table 5.5. Compared to less than 100$/ton fly ash prices, the average price for magnesium oxide is 300 $/ton, potassium dihydrogen phosphate is 1,000 $/ton, and boric acid is about 1,200 $/ton. Unfortunately, the composition of the proposed MKPC

formulations includes 50 wt. % of these expensive raw materials. That is why MKPC cements are much more expensive than Portland cement and economically not viable for the oil and gas industry.

Unfortunately, the high cost of raw materials causes a disadvantage and limits the application of these cements severely as a substitute for Portland cement. This is probably one of the reasons why any application of MKPC for permafrost to shallow wells has not been reported yet. However, it is clear from the cost comparison in this study that the oil industry will rely on conventional cement systems, and the application of MKPC cements may only be seen if the benefits outweigh the costs in this cost-conscious world.

Materials Name	Price Range ; Source for Price
Magnesium oxide	Invoice: 48.41 $/kg; 200-500 $/ton; Alibaba.com
Potassium phosphate	Invoice: 67.5 $/kg; 800-1200 $/ton; Alibaba.com
Boric Acid	Invoice: 47.1 $/kg; 500-2000 $/ton; Alibaba.com
C Class Fly Ash	50-100 $/ton; Alibaba.com
Portland Cement	30- 70 $/ton; Alibaba.com
Water	Average taken as 0.5 $/bbl

Table 5.4: Average bulk prices for raw materials as of April 2018.

Cement Type	Lowest Cost $/bbl	Average Cost $/bbl	Highest Cost $/bbl
Portland Cement	6	10	15
Acrylic Cement	81	109	137

Table 5.5: Cost comparison by average material prices as of April 2018.

ADDITIONAL NOTES ON THE EXPERIMENTS

This section will provide additional information and critical findings on the experiments.

Sensitivity on Reactivity of Magnesium Oxide

The reactivity of the magnesium oxide affects the amount of heat generated and the setting time of the slurry remarkably. As the reactivity decreases, the heat of formation decreases, and thickening time increases. The lowest temperature rise has been observed by using dead burnt heavy powder magnesium oxide, particularly M68-3 heavy powder among the magnesium oxide grades used throughout the experiments.

Free Water and Ability to Set Under Water

In general, slurries containing boric acid resulted in negligible amounts of free water. For this reason, no free water test has been conducted. However, salt addition causes an increase in free water amount.

The slurries tested in the laboratory conditions can set under water. The molds half filled with cement slurry have been filled up with tap water and cured at room temperature, and they still set well under water.

Contamination of Raw Materials

Magnesium Carbonate Hydroxide Tetrahydrate ($4MgCO_3.Mg(OH)_2.4H_2O$) was once used by mistake during the experiments as magnesium oxide powder. Upon use of this chemical, detrimental results have been observed in terms of volumetric expansion. Beside high porosity in cement samples, they did not set and hence did not achieve any compressive strength.

Effect of Thinners

Thinners such as Potassium Lignite (K-Lig), Q-Broxin (a dispersant and filtration control agent), and carbonax (unmodified lignite) have been added into the cement slurry to enhance easy pumping and reduce the viscosity of the cement slurry. Contrary to expectations, the addition of these thinners shortened the thickening time of the slurry rather than improving the rheological properties of the slurry. However, they slightly enhanced the compressive strength development. Thickening time and compressive strength results with thinners are presented in Table 5.6 where reference sample has previously achieved 1:30 hours of thickening time without thinners. Maximum thickening time was recorded as 1:17 hours by using the above-mentioned thinners. In addition to the thinners tabulated in Table 5.6, Chrome Free Lignosulphonate (CFL) was also added to cement slurry at 4 wt. %, but the compressive strength of samples failed to achieve 500 psi, thus the results with CFL addition are not presented in Table 5.6.

MgO	KH_2PO_4	F Fly Ash	Additives					Thick. Time	Comp. Strength
			Boric Acid	Salt	K-Lig	Q-Brox	Carbonax		
(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(hr:min)	(psi)
12.5	37.5	50	3	3	1	-	-	0:43	1100
					4	-	-	1:03	850
					12	-	-	0:47	1200
					-	4	-	1:07	900
					-	12	-	0:50	700
					-	-	4	1:17	1000
					-	-	12	1:00	850

Table 5.6: Thickening time results for various proportions of thinners in slurry.

Replacement of Boric Acid by Hydrochloric Acid

In the literature, boric acid, borax and boron components are frequently used to retard the setting time of these cements. However, boric acid is a weak acid and partially soluble in water. Thus, some boric acid crystals remain undissolved in water. The agitation and generated heat through the slurry preparation process probably help complete dissolution of boric acid crystals in the slurry. Later, it was decided to check effects of a more acidic environment on the solubility of the magnesium oxide and potassium phosphate. For this reason, boric acid was replaced by hydrochloric acid and added to slurry in a trial and error approach. The reference sample employed 3 wt. % boric acid in the slurry. Then, boric acid was first replaced by 1.3 wt. % hydrochloric acid (37.7% Assay), and thickening time has been recorded as 1:25 hours with 500 psi compressive strength after 24 hours. The test was repeated with 2.6 wt. % hydrochloric acid, and thickening time has dramatically reduced to 33 minutes with 450 psi compressive strength after 24 hours. Ultimately, thickening time and compressive strength were negatively affected with increasing acidity.

Effect of Increasing Temperature

Curing temperature plays an important role in setting time and compressive strength development. As temperature increases, any MKPC formulation sets in much faster and develops higher compressive strengths. In the literature, MKPC formulations, which were cured at near zero temperatures by simulating the arctic environments, achieved thickening times up to 5 hours. Consequently, curing cement samples at higher temperatures i.e. 72 ºF, is probably the main reason for not achieving such long thickening time even with greater amounts of boric acid and/or salt in the composition.

Further experiments were conducted to analyze the effects of temperature through this study. The cement slurries with compositions in Table 5.7 were mixed in a Pyrex, heatproof glass container at 155 ºF by using a magnetic stirrer with bottom heat element. Top plate temperature and rpm of the stirrer were kept constant at 155 ºF and around 200 rpm to 250 rpm, respectively. Results presented in Table 5.7 indicate that increasing temperature dramatically reduces thickening time while enhancing compressive strength development. For example, sample with 10 wt. % boric acid yields 1:35 hours thickening time at 72 ºF, and it achieves only 33 minutes at 155 ºF. It is highly probable that same composition would achieve a considerably longer thickening time if cured at near zero/subzero temperatures. Similarly, Portland cement mixtures with 4 wt. % bentonite and 5 wt. % salt were also tested at 155 ºF under atmospheric pressure to see the effects of increasing temperature on thickening time and compressive strength. The reference data shown in Table 5.8 was taken from Halliburton Red Book (Halliburton, 2011). The results are provided in Table 5.9 where thickening time has been dramatically reduced from a few hours to nearly 20 to 25 minutes at 155 ºF in all three cases; Portland cement, Portland cement with 4 wt. % bentonite, and Portland cement with 5 wt. % salt. Ultimately, increasing temperature significantly reduces thickening time and setting time.

MgO	KH_2PO_4	C Fly Ash	Additives		Water	Thickening Time	Comp. Strength	Curing Temperature
			Boric Acid	HR5				
(g)	(g)	(g)	(g)	(g)	(g)	(hr:min)	(psi)	(ºF)
12.5	37.5	50	5	5	38.5	1:50	500	72 ºF
						0:20	750	155 ºF
			10	5		1:35	800	72 ºF
						0:33	950	155 ºF

Table 5.7: Effect of increasing temperature on thickening time & compressive strength.

Thickening Time	API Casing Tests			API Squeeze Tests		
% Bentonite	4000'	6000'	8000'	2000'	4000'	6000'
0	3:00+	2:25	1:40	2:14	1:32	1:01
4	2:34	1:57	1:32	2:26	1:18	0:58
Thickening Time and Compressive Strength						
	API Casing Tests			Compressive Strength		
% Salt	2000'			(110 ºF & 1600 psi)		
0	4:15			3230		
5	2:30			4350		

Table 5.8: Data for thickening time and compressive strength (Halliburton, 2011).

Magnetic Stirrer at 155 ºF, 200-250 rpm, atmospheric pressure				
Type of Cement	Compressive Strength (psi)			Thickening Time (hr:min)
Portland Cement	1775	2025	2100	0:20
4 % Bentonite	1200	1250	1275	0:25
5 % Salt	2350	3000	3100	0:22

Table 5.9: Results for thickening time and compressive strength at 155 ºF.

Chapter 6: Summary, Conclusions and Future Recommendations

In this study, chemically bonded phosphate cements (CBPC) have been studied with a primary focus on magnesium potassium phosphate cements (MKPC). Properties of magnesium potassium phosphate cements are revealed in detail through available experimental data in the literature, and further experiments are conducted to achieve new formulations for the oil and gas industry. Chemical reactions between dead burnt magnesium oxide (MgO) and potassium dihydrogen phosphate (KH_2PO_4) at ambient temperatures forms ceramic like cements within minutes (typically in less than an hour), and they demonstrate superior mechanical properties with hardness and durability of cements and ceramics. It is possible to formulate new MKPC systems with different additives to meet the demanded properties on cements. That is why these acrylic cements are regarded as prospective novel cement systems as a substitute for Portland cement systems in fields where the benefits outweigh the costs. Consequently, these materials have successfully found applications in various fields such as radioactive and hazardous waste encapsulation, biomedical fields, dental and clinical treatments, and in civil engineering structural materials. Short setting time and heat of hydration (heat generated) during the formation of these cements and the high cost of raw materials are considered as major disadvantages for many applications. These disadvantages can be overcome by developing new formulations with further control on setting time and heat of hydration, and by employing less expensive byproducts/additives in the composition.

Good well cementing practices require a minimum of two hours thickening time and 500 psi compressive strength development in 24 hours in compliance with API standards. This study takes off from existing literature and concentrates on achieving sufficiently long thickening time and enough compressive strength at 72 ºF and under

atmospheric pressure. As a result, a few formulations are proposed as candidate wellbore sealants applicable to well cementing jobs in the oil and gas industry, and they are provided in Table 6.1. Contrary to previously proposed formulations for permafrost wells, they employ significantly greater amounts of boric acid and up to 1 wt. % salt in the composition. It is necessary to note that excess amounts of both boric acid and salt in the composition can negatively affect the final mechanical properties. Thus, optimum amounts of additives should be present in the composition.

Form.	MgO	KH_2PO_4	C Class Fly Ash	Additives		Water	Thickening Time	Comp. Strength
				Boric Acid	Salt			
#	(g)	(g)	(g)	(g)	(g)	(g)	(hr:min)	(psi)
1	12.5	37.5	50.0	3.0	1.0	38.5	3:27	775
2	12.5	37.5	50.0	2.5	1.0	38.5	2:44	850
3	12.5	37.5	50.0	5.0	-	38.5	2:36	510
4	12.5	37.5	50.0	4.0	-	38.5	2:30	575

Table 6.1: Proposed MKPC formulations at 72 ºF under atmospheric pressure.

Importantly, the cost analysis conducted in this study indicates that application of these cements is not very feasible as borehole sealants because they are nearly 10 times more expensive than Portland cement. However, the ability to set within hours implying shorter wait on cement time (WOC) can allow companies to resume their drilling operations sooner. This might balance the high costs associated with these cements, especially at expensive operating conditions. Ultimately, future work can focus on achieving a detailed feasibility analysis to shed light on the applicability of them in the oil and gas industry.

In addition to high costs associated with MKPC, the heat of formation can be an issue especially for permafrost wells in arctic regions. MKPC have already been stated as superior zonal isolators with low thermal conductivities in the literature. However, temperature evolution section of this study reveals a dramatic temperature rise and considerable heat of hydration. Thus, additional research on temperature evolution and thermal conductivity should be conducted. After all, MKPC can be utilized safely as wellbore sealants at permafrost wells to avoid thawing of permafrost around the wellbore. Finally, superior mechanical properties i.e. low thermal conductivity, good zonal isolation, and bonding characteristics may lead utilization of these cements at wells in heavy oil reservoirs with steam injection/production activities and in geothermal fields to prevent heat losses. However, considering the high bottom hole temperatures encountered in geothermal wells, it is critical to conduct further research to check if these cements flash set or not at elevated temperatures.

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